

THE ACTIVATION OF CARBON MONOXIDE AND CARBON  
DIOXIDE BY TRANSITION METAL CARBONYL COMPLEXES

BY

KEITH D. WEISS

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To my mother and father

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By

Keith D. Weiss

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Chairman: Russell S. Drago  
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The development of new carbon resources to be used either as fuels or as chemical feedstocks has been of major concern to the industrial community since the oil shortage in the early 1970s. In this respect, a lot of activity has been observed over the past decade concerning the binding and activation of carbon dioxide and carbon monoxide. The emphasis in this work has been upon the activation of carbon dioxide and carbon monoxide by transition metal complexes.

The first study involved the binding of carbon dioxide to a variety of transition metal carbonyl anions. It was found that the nucleophilicity of the metal center greatly affected the coordination of carbon dioxide. This work then was extended into an investigation of the low pressure reduction of carbon dioxide to methyl formate by a rhenium carbonyl catalyst. Infrared spectroscopy was used to characterize the active species and probe the mechanism of the reaction. It was found that this rhenium carbonyl



system was more effective towards the reduction of carbon monoxide than carbon dioxide.

The second study dealt with the conversion of synthesis gas and  $\text{HCl(g)}$  to methyl chloride under mild temperatures and pressures by a supported iridium carbonyl catalyst. Several different routes to methyl chloride were identified within the system. Infrared spectroscopy was used to identify the active species in the reaction and investigate their various modes of deactivation. It was shown that discrete iridium carbonyl complexes existed under the employed reaction conditions. Finally, a mechanism for the formation of methyl chloride in this system was proposed. This study concluded with an examination of other supported metal carbonyl catalysts. It was found that a change in the composition of the metal catalyst could alter the activity and selectivity of the reaction. In this respect, a supported ruthenium carbonyl catalyst was observed to be active towards the formation of ethyl chloride and various other two-carbon products.

## CHAPTER I

### INTRODUCTION

With the oil shortage in the 1970s, there was great interest in the development of alternative carbon resources to be used as fuels and chemical feedstocks. Although the oil shortage has receded for the time being, the problem has not been resolved. The reoccurrence of a fuel shortage is predicted for the economy of the future. One new carbon resource would involve the gasification of coal into a mixture of carbon monoxide and hydrogen known as synthesis gas.<sup>1</sup> Since there is an abundance of coal reserves, the utilization of synthesis gas as a chemical feedstock or fuel could hold future economic advantages. Another untapped carbon reserve is the carbon dioxide released into the atmosphere as an industrial waste product. Carbon dioxide has the ability to absorb infrared radiation which is predicted to give rise to an increase in global temperature commonly referred to as the "Greenhouse Effect".<sup>2,3</sup> Although other gases can initiate a similar temperature rise, the most abundant gas in the atmosphere to produce this effect is carbon dioxide.<sup>4</sup> Recycling carbon dioxide waste by utilizing it as an inexpensive chemical feedstock would decrease the amount of the gas released into the atmosphere.

There are several methods that can be used to investigate the activation of carbon monoxide and carbon dioxide. These methods range from mechanistic studies of biological or natural systems, such as hemoproteins,<sup>5</sup> carbonic anhydrase<sup>6</sup> and photosynthesis<sup>7</sup> to the investigation of the interaction of carbon monoxide and carbon dioxide with metal complexes in organometallic reactions. Currently over 90% of the commercial chemical processes are catalytic in nature.<sup>8</sup> Since many of these commercial processes employ either metals (heterogeneous) or metal complexes (homogeneous) as catalysts, a logical starting point for the development of carbon monoxide and carbon dioxide as a chemical feedstock or fuel is a study of their interaction with transition metal complexes.

Reported here are the results of two studies involving an evaluation of the feasibility of binding and activating carbon dioxide and carbon monoxide by transition metal carbonyl complexes. The first study involves the binding of carbon dioxide to transition metal carbonyl anions with varying degrees of nucleophilic metal centers. The results obtained aid in the understanding of the interaction of carbon dioxide with transition metal catalysts, as well as the effect that residual contaminants, such as water, may have on carbon dioxide activation. This study concludes with an investigation of the catalytic behavior of the corresponding transition metal carbonyl hydrides towards carbon dioxide reduction. Primarily, the low temperature

and low pressure reduction of carbon dioxide and hydrogen in alcohol solvents to alkyl formates was investigated.

The second study involves the low temperature and low pressure reduction of carbon monoxide by "heterogenized" homogeneous catalysts. The mechanism of a novel system employing a supported tetrairidium carbonyl cluster as catalyst for the conversion of carbon monoxide, hydrogen and hydrogen chloride to methyl chloride was studied by infrared spectroscopy. The commercial feasibility of this system was evaluated through the optimization of the different system parameters, such as temperature and residence time.

CHAPTER II  
ACTIVATION OF CARBON DIOXIDE

Background

The thermodynamic stability of carbon dioxide is the primary reason it is an "oxygen sink" or waste product in many commercial chemical processes. However, the two unsaturated double bonds in carbon dioxide make it theoretically possible to convert carbon dioxide into organic products. This is supported by the thermodynamic feasibility of many reactions involving carbon dioxide<sup>9</sup> as shown in Table 2-1. Furthermore, carbon dioxide is used as

Table 2-1. Enthalpy Changes in Reactions Involving Carbon Dioxide

<u>Reaction</u>	<u><math>\Delta H^\circ</math></u>
$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-31.3
$\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-60.5
$2\text{CO}_2(\text{g}) + 6\text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OCH}_3(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	-60.9
$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) + \text{CH}_3\text{OH}(\text{l}) \longrightarrow \text{HCO}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$	-7.7
$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) + \text{CH}_3\text{OH}(\text{l}) \longrightarrow \text{CH}_3\text{CO}_2\text{H}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-33.0
$\text{CO}_2(\text{g}) + \text{CH}_4(\text{g}) \longrightarrow \text{CH}_3\text{CO}_2\text{H}(\text{l})$	-3.8
$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) + \text{C}_2\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_5\text{CO}_2\text{H}(\text{l})$	-40.6

$\Delta H^\circ$  data given as kcal mole<sup>-1</sup>.

a chemical feedstock in the commercial production of salicylic acid,<sup>10,11</sup> urea<sup>12,13</sup> and terephthalic acid.<sup>14</sup> Unfortunately, the existence of a kinetic barrier in many reactions involving carbon dioxide prevents these reactions from spontaneously occurring. These reactions may occur if the activation energy associated with this kinetic barrier can be lowered through the binding of carbon dioxide to a metal catalyst.

There have been a variety of literature review articles dedicated to the binding and activation of carbon dioxide.<sup>9,15-22</sup> Several possibilities exist for the interaction of carbon dioxide with a metal center.<sup>18,23</sup> One mode of binding is a donor-acceptor type complex termed "end-on" formed by electron pair donation from the oxygen's highest occupied molecular orbital (HOMO) to the corresponding metal d orbital as shown in Figure 2-1. A "c-coordination" mode of binding involving a dative interaction or transfer of two electrons from the metal atom to the lowest unoccupied molecular orbital (LUMO) of carbon dioxide also may occur. Finally, a third possible mode of binding referred to as "side-on" is a combination of the interaction of the HOMO of carbon dioxide with a vacant metal d orbital and the simultaneous transfer of metal  $\sigma$  electrons to the vacant LUMO of carbon dioxide. The high electron affinity of carbon dioxide suggests that the existence of the "side-on" and "c-coordination" modes of binding should be more favorable than the "end-on" mode.

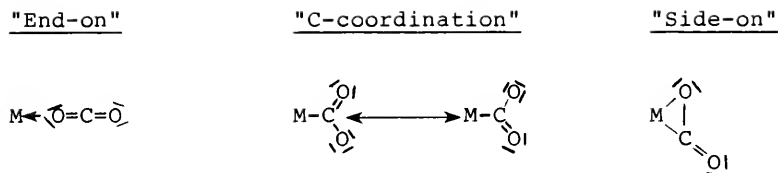


Figure 2-1. Modes of Binding for Carbon Dioxide with a Metal Center

This is supported by the favorability of "side-on" > "c-coordination" >> "end-on" reported in several molecular orbital investigations.<sup>24-28</sup> These studies point out that the favorability of "c-coordination" may be enhanced by the presence of a counter ion which can interact with the electron density surrounding the oxygen atoms of the bound carbon dioxide. Further evidence is provided by the limited number of x-ray structures that have been obtained for bound carbon dioxide complexes as shown in Table 2-2. Many other complexes have been reported to bind carbon dioxide as suggested by infrared spectroscopy.<sup>9</sup>

Although the "side-on" mode of coordination is the most favorable, the "c-coordination" mode is very important for catalysis. Metal-carbon bond formation may lead either to the growth of carbon-carbon chains through insertion reactions or to the catalytic formation of formate species through hydrogenolysis. To date there has been only limited success involving the catalytic reduction of carbon dioxide. The first example of the catalytic reduction of carbon dioxide was the conversion of an amine to a formamide

Table 2-2. Modes of Carbon Dioxide Binding for Complexes with Geometry Determined by X-ray Crystallography

<u>Bound Carbon Dioxide Complex</u>	<u>Mode of Binding</u>	<u>References</u>
(py)Co(salen)K(CO <sub>2</sub> )	c-coordination	29
Rh(diars) <sub>2</sub> (CO <sub>2</sub> )Cl	c-coordination	30
[HOS <sub>3</sub> (CO) <sub>10</sub> (O <sub>2</sub> C)Os <sub>6</sub> (CO) <sub>17</sub> ] <sup>-</sup>	c-coordination <sup>a</sup>	31
[(OC) <sub>5</sub> Re(CO <sub>2</sub> )Re(CO) <sub>4</sub> ] <sub>2</sub>	c-coordination <sup>a</sup>	32
Ni(CO <sub>2</sub> )(PCY <sub>3</sub> ) <sub>2</sub>	side-on	33
Nb(n-C <sub>5</sub> H <sub>4</sub> Me) <sub>2</sub> (CH <sub>2</sub> SiMe <sub>3</sub> )(CO <sub>2</sub> )	side-on	34
IrCl(C <sub>2</sub> O <sub>4</sub> )(PMe <sub>3</sub> ) <sub>3</sub> -0.5•C <sub>6</sub> H <sub>6</sub>	Combination of modes	35

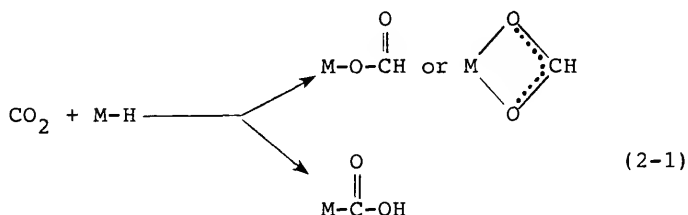
a = Complex not formed directly from carbon dioxide(g).

employing either IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> or CuCl(PPh<sub>3</sub>)<sub>3</sub> as catalyst.<sup>36</sup> It was proposed that the mechanism for this reaction proceeded through the insertion of carbon dioxide into a metal-hydrogen bond.<sup>9</sup>

The interaction of carbon dioxide with a transition metal hydride may proceed through two different reaction pathways. Carbon dioxide insertion into a metal-hydrogen bond will lead to either the formation of a formate complex or to a metallocarboxylic acid derivative as shown in Equation 2-1. Although the formation of metallocarboxylic acid complexes has been reported for reactions between carbon monoxide with a metal hydroxide complex<sup>37</sup> and for hydroxide ion with a metal carbonyl complex,<sup>38-42</sup> there has been no direct evidence for the formation of a metallocar-

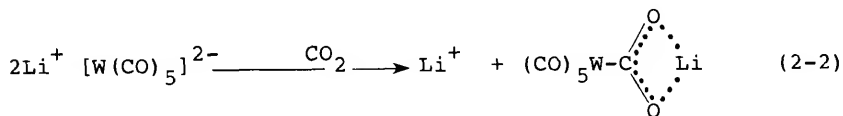


boxylic acid derivative through the insertion of carbon dioxide into a metal hydride bond. The isolation of organic products in several reactions has suggested the possibility



of a metallocarboxylic acid intermediate.<sup>43</sup> On the other hand, the formation of formate intermediates has been observed for carbon dioxide reactions with metal hydride complexes.<sup>44,45</sup>

It is possible that metal-carbon bond formation can be enhanced by altering the nucleophilicity of the metal center in a transition metal carbonyl hydride complex. It has been shown by infrared and carbon-13 NMR spectroscopy that alkali metal salts of transition metal carbonyl hydrides can bind carbon dioxide through the "c-coordination" mode as shown in Equation 2-2.<sup>46</sup> There are several added advantages for the interaction of carbon dioxide with a transition metal



complex. First, many carbonyl complexes activate hydrogen under mild conditions to produce metal carbonyl hydride complexes.<sup>47</sup> Since the reduction of carbon dioxide requires

a source of hydrogen, the ability to bind carbon dioxide and activate hydrogen gas by the same transition metal complex would be advantageous. There also have been recent reports of transition metal carbonyl complexes reducing carbon dioxide to carbon monoxide<sup>48</sup> and to alkyl formates.<sup>49</sup>

An evaluation of the feasibility of binding carbon dioxide through metal-carbon bond formation can be accomplished by an investigation of the interaction of carbon dioxide with the alkali metal salts of transition metal carbonyl hydride complexes whose  $K_a$  values or metal nucleophilicities are known. The  $K_a$  and nucleophilicity data for the complexes to be investigated are summarized in Table 2-3. The available literature has indicated that several of these anions do interact with carbon dioxide.<sup>48,50,51</sup> For instance, the formation of iron pentacarbonyl and sodium carbonate has been reported to occur for the reaction of carbon dioxide with  $\text{Na}_2\text{Fe}(\text{CO})_4$ .<sup>48</sup> It also has been reported that carbon dioxide reacts with  $\text{NaMn}(\text{CO})_5$  to form sodium bicarbonate and an unidentified manganese complex.<sup>50</sup> More recently, preliminary solution infrared data were interpreted in a Russian report to suggest that both  $\text{NaRe}(\text{CO})_5$  and  $\text{NaMn}(\text{CO})_5$  stabilize the formation of a "c-coordination" bound carbon dioxide complex as shown in Equation 2-3.<sup>51</sup> The addition of methyl iodide to this carbon dioxide bound complex was reported to result in the formation of  $[(\text{CO})_3\text{M}(\text{CO}_2\text{CH}_3)]_2$  by methyl cation

addition to an oxygen of the bound carbon dioxide. After evaluation of the feasibility of binding carbon dioxide to transition metal anions, a logical extension of this work

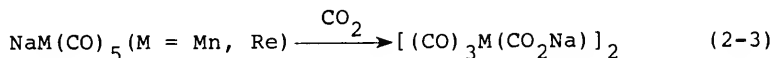
Table 2-3. Acid Dissociation Constants for Metal Carbonyl Hydrides and the Nucleophilicities of the Corresponding Anions

Hydride Complex	$K_a(\text{H}_2\text{O})^a$	Anion	Nucleophilicity <sup>b</sup>
$\text{HCo}(\text{CO})_4$	<2	$\text{Co}(\text{CO})_4^-$	1
$\text{H}_2\text{Fe}(\text{CO})_4$	$3.6 \times 10^{-5} (K_1)$ , $1.0 \times 10^{-14} (K_2)$	$\text{Fe}(\text{CO})_4^{2-}$	-
$\text{HMn}(\text{CO})_5$	$8 \times 10^{-8}$	$\text{Mn}(\text{CO})_5^-$	77
$\text{HRe}(\text{CO})_5$	"Very weakly acidic"	$\text{Re}(\text{CO})_5^-$	25,000

a =  $K_a$  data obtained from reference 52;

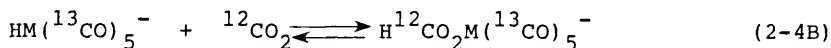
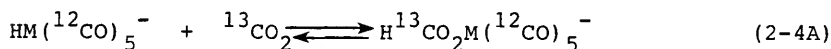
b = Nucleophilicity data obtained from reference 53.

would be an investigation into the catalytic behavior of these complexes towards carbon dioxide reduction.



Recall that the first example of the catalytic reduction of carbon dioxide was the conversion of an amine to a formamide.<sup>36</sup> It was found that replacement of the amine with an alcohol produced a formic ester as the primary product.<sup>54</sup> Since then there have been several reports indicating the formation of metalloformate derivatives through the interaction of carbon dioxide with group 6B

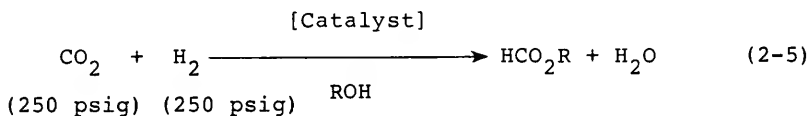
metal carbonyl anions and hydrides.<sup>46,50,55-57</sup> The reduction of carbon dioxide to carbon monoxide by group 6B metal carbonyl anions,  $\text{Li}_2[\text{M}(\text{CO})_5]$ , has been shown to occur by the formation of lithium carbonate and the corresponding group 6B metal hexacarbonyl complex,  $\text{M}(\text{CO})_6$ .<sup>46</sup> Carbon-13 labeling studies involving the reversible binding of carbon dioxide to group 6B metal carbonyl hydrides, as shown in Equation 2-4 (A-B), demonstrate that carbon dioxide is not reduced to carbon monoxide at atmospheric pressure by these complexes.<sup>57</sup> A mechanism for the intramolecular conversion of a metalloformate complex to a metallocarboxylic acid complex would most likely proceed through the reduction of the bound carbon dioxide to bound carbon monoxide followed by the addition of hydroxide ion to a carbonyl ligand. Therefore, these carbon-13 labeling studies also suggest



that the metalloformate complex does not intramolecularly convert to a metallocarboxylic acid species.<sup>58</sup> Although the formation of metallocarboxylic acid species has not been reported to occur in reactions between carbon dioxide and metal hydrides, they have been reported to form as intermediates in reactions between group 6B metal

hexacarbonyls and hydroxide ions en route to the formation of a metal hydride anion and carbon dioxide.<sup>57</sup> It is possible that the relative stability of  $M(\text{COOH})$ ,  $M(\text{O}_2\text{CH})$  or  $M(\text{OCHO})$  could be influenced by an alteration in the nucleophilicity of the metal center.

Equation 2-5 illustrates that at elevated pressures in alcohol solvents the group 6B metal carbonyl hydrides catalytically reduce carbon dioxide to alkyl formates and water.<sup>49</sup> The predominate species in solution during



catalysis were determined through the interpretation of infrared data to be  $M(\text{CO})_6$  and  $\text{HCO}_2M(\text{CO})_5^-$ . The existence of hydrogen bonding between the alcohol solvent and the metalloformate intermediate also was suggested in the interpretation of these infrared data. The  $\text{HCO}_2M(\text{CO})_5^-$  intermediate was proposed to be the catalytically active species since  $M(\text{CO})_6$  was found to be catalytically inactive. The proposed mechanism<sup>49</sup> for this reaction shown in Figure 2-2 suggests that it is actually formic acid which is produced catalytically. The alcohol solvent then reacts with this formic acid to form the alkyl formate and water. This mechanism is supported in the identification of formic acid by gas chromatography in reactions where benzene has replaced the alcohol as solvent. A decrease in activity was

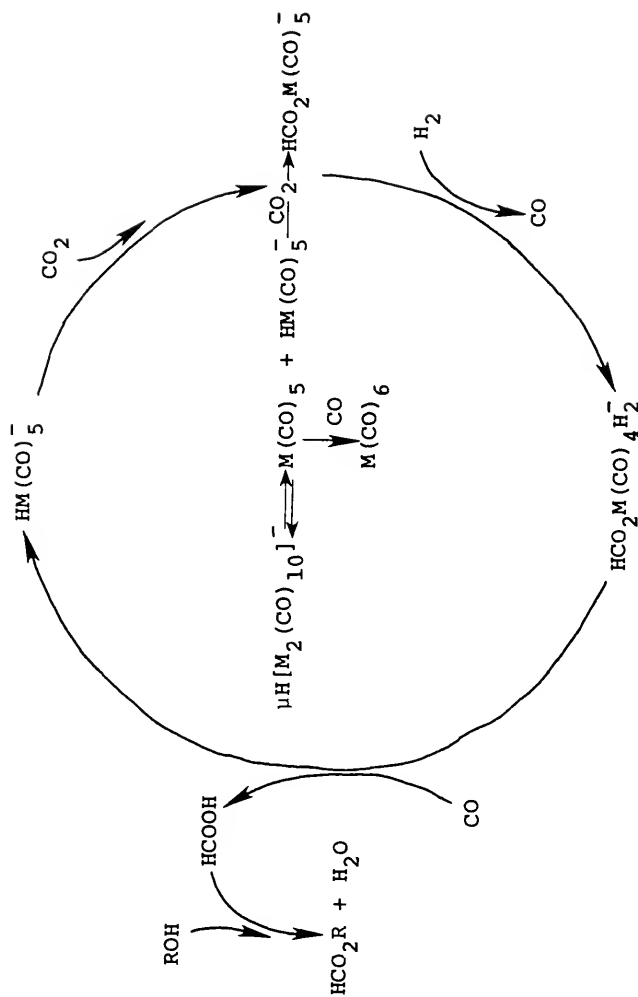


Figure 2-2. A Proposed Mechanism for the Reduction of Carbon Dioxide to Alkyl Formates by Group 6B Metal Carbonyl Hydrides

observed for the formation of ethyl formate as compared to methyl formate in the corresponding alcohol solvent. This effect has been proposed to be due to the increased coordinating ability of ethanol inhibiting the oxidative addition of hydrogen by the metalloformate intermediate.

The catalytic activity of systems capable of converting carbon dioxide into alkyl formates is summarized in Table 2-4. The activity of group 6B metal carbonyl hydrides compares very closely to the activity for carbon dioxide reduction to alkyl formates using ruthenium<sup>59</sup> or iron<sup>54</sup> carbonyl hydrides as catalysts. Similar activity also has been established for systems utilizing group VIII metal phosphine complexes with either  $\text{BF}_3$  or a tertiary amine as cocatalyst.<sup>60,61</sup> Although  $\text{HFe}_3(\text{CO})_{11}^-$  and  $\text{HFe}(\text{CO})_4^-$  have not been reported to bind carbon dioxide at atmospheric pressure these species catalyze the formation of methyl formate.<sup>54</sup> The catalytic formation of methyl formate in alcohol solvents was found to follow a general trend of increasing activity with an increase in temperature, pressure or reaction time. Infrared spectroscopy was used to identify the formation of carbonate and iron penta-carbonyl during the reaction. This reaction was proposed to be very selective for methyl formate formation since no other low molecular weight products could be identified by gas chromatography.<sup>54</sup> The predominant species present in reactions involving ruthenium carbonyl hydrides as catalysts was identified by infrared spectroscopy to be

Table 2-4. A Summary of Catalyst Activity for the Reduction of Carbon Dioxide to Alkyl Formates

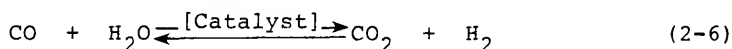
<u>Catalyst</u>	<u>Turnover Number</u> <sup>a</sup>	<u>Reference</u>
$\mu\text{-H}[\text{W}_2(\text{CO})_{10}]^-$	14.7	49
$\text{HCO}_2\text{W}(\text{CO})_5$	16.4	49
$\text{W}(\text{CO})_6$	-	49
$\mu\text{-H}[\text{Cr}_2(\text{CO})_{10}]^-$	14.5	49
$\text{HCO}_2\text{Cr}(\text{CO})_5^-$	14.6	49
$\text{HRu}_3(\text{CO})_{11}^-$	4.1	59
$\text{HCO}_2\text{Ru}_3(\text{CO})_{10}^-$	5.7	59
$\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$	7.3	59
$\text{Ru}_3(\text{CO})_{12}$	<0.3	59
$\text{HFe}_3(\text{CO})_{11}^-$	5.2	54
$\text{HFe}(\text{CO})_4^-$	2.0	54
$\text{Pd}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$	23.0 <sup>b</sup>	60
$\mu\text{-H}[\text{W}_2(\text{CO})_{10}]^-$	5.1 <sup>c</sup>	49
$\text{HCO}_2\text{W}(\text{CO})_5$	3.8 <sup>c</sup>	49
$\text{HCO}_2\text{Ru}_3(\text{CO})_{10}^-$	4.1 <sup>c</sup>	59

Reaction ConditionsRef. 49:  $\text{CO}_2$  (250 psi) +  $\text{H}_2$  (250 psi) at 125°C for 24 hoursRef. 59:  $\text{CO}_2$  (250 psi) +  $\text{H}_2$  (250 psi) at 125°C for 24 hoursRef. 54:  $\text{CO}_2$  (300 psi) +  $\text{H}_2$  (300 psi) at 150°C for 24 hoursRef. 60:  $\text{CO}_2$  (350 psi) +  $\text{H}_2$  (350 psi) at 140°C for 21 hours

<sup>a</sup>Turnover = mole of  $\text{HCO}_2\text{CH}_3$ /mole of catalyst; <sup>b</sup> $(\text{CH}_3)_3\text{N}$  used as cocatalyst; <sup>c</sup>Addition of  $\text{CO}$  (100 psi) to reactant gases.



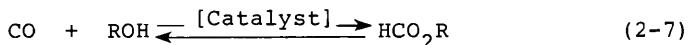
$\text{H}_3\text{Ru}_4(\text{CO})_{12}$ .<sup>59</sup> It was suggested that these reactions also could lead to the formation of carbon monoxide through the reverse of the water-gas shift reaction as shown in Equation 2-6. It is possible that the observed formation of the alkyl formate may have resulted from the reduction of carbon monoxide. However, the addition of carbon monoxide to the carbon dioxide-hydrogen gas mixture in these reactions was



observed to inhibit the formation of alkyl formates.<sup>59</sup> A similar retarding effect upon carbon monoxide addition was observed in the activity of the group 6B metal carbonyl hydrides towards alkyl formate formation. It was concluded that this observed decrease in activity towards the formation of alkyl formates demonstrated that the reduction of carbon dioxide in these reactions did not proceed through the formation of carbon monoxide.<sup>49</sup> This was further substantiated by gas chromatographic detection of less than 0.05% carbon monoxide in the  $\text{CO}_2\text{-H}_2$  reaction gas mixture. This amount was reported to be far below the equilibrium distribution of carbon monoxide expected for the reverse of the water-gas shift reaction.

The preceding conclusion is in contradiction to recent reports which indicate that carbon monoxide will react with either tungsten carbonyl<sup>62</sup> or ruthenium carbonyl<sup>59</sup> hydrides in methanol to yield methyl formate as shown in Equation

2-7. As shown in Table 2-5, the activity for a reaction utilizing carbon monoxide is vastly increased over the same reaction using a  $\text{CO}_2\text{-H}_2$  mixture. In fact, the addition of carbon dioxide or hydrogen to the carbon monoxide reactant gas has been found to inhibit the formation of methyl



formate. Tungsten hexacarbonyl was identified by infrared spectroscopy to be the predominant carbonyl species present in the reactions involving a tungsten carbonyl hydride and carbon monoxide.<sup>62</sup> Although tungsten hexacarbonyl is inactive as a catalyst precursor, the addition of potassium methoxide to this reaction produces methyl formate in high yields. A mechanism consistent with the preceding observations has been proposed for the reduction of carbon monoxide to methyl formate in a methanol solvent.<sup>62</sup> This mechanism, shown in Figure 2-3, strongly suggests the interaction of a methoxide anion with  $\text{W}(\text{CO})_6$  to produce the active catalytic species,  $\text{CH}_3\text{OW}(\text{CO})_5^-$ .

The synthesis of methyl formate from carbon dioxide or carbon monoxide is important because methyl formate is used to synthesize several organic chemicals, such as formic acid, acetic acid, formamide, ethylene glycol and formaldehyde.<sup>63-65</sup> Since most of these are important commercial commodity chemicals, the formation of methyl formate from carbon monoxide or carbon dioxide could be

Table 2-5. A Summary of Catalyst Activity for the Reduction of Carbon Monoxide to Alkyl Formates

<u>Catalyst</u>	<u>Turnover Number<sup>a</sup></u>	<u>Reference</u>
$\mu\text{-H[W}_2(\text{CO})_{10}]^-$	269	62
$\text{HCO}_2\text{W}(\text{CO})_5$	185	62
$\text{CH}_3\text{W}(\text{CO})_5$	305	62
$\text{W}(\text{CO})_6$	-	62
$\text{W}(\text{CO})_6/\text{KOCH}_3$	333	62
$\text{KOCH}_3$	50	62
$\text{H}_3\text{Ru}_3(\text{CO})_{11}^-$	106	59
$\text{H}_3\text{Ru}_3(\text{CO})_{12}^-$	88	59
$\text{H}_3\text{Ru}_3(\text{CO})_{11}^-$	40 <sup>b</sup>	59
$\text{W}(\text{CO})_6/\text{KOCH}_3$	- <sup>c</sup>	62

Reaction Conditions

Ref. 62: CO (250 psi) at 125°C for 24 hours

Ref. 59: CO (250 psi) at 125°C for 24 hours

<sup>a</sup>Turnover Number = mole of  $\text{HCO}_2\text{H}_3$ /mole of catalyst;

<sup>b</sup>Addition of  $\text{H}_2$  (250 psi) to reactant gas;

<sup>c</sup>Addition of  $\text{CO}_2$  (25 psi) to reactant gas.

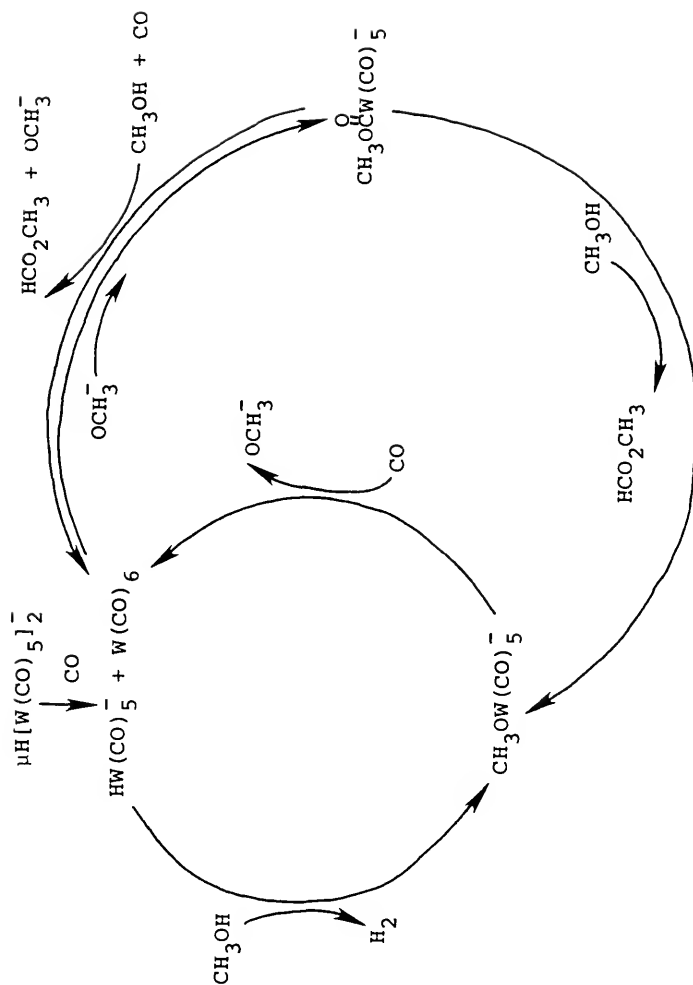


Figure 2-3. A Proposed Mechanism for the Reduction of Carbon Monoxide to Methyl Formate by Tungsten Carbonyl Complexes

industrially useful. This industrial importance coupled with a fundamental interest in the activation of  $\text{CO}_2$  and CO justifies further research into the formation of alkyl formates from the reduction of carbon dioxide or carbon monoxide by metal carbonyl complexes. The final justification for further careful fundamental work in this area arises from the contradictory results that have been reported in the literature.

### Experimental

#### Reagents

All metal complexes were used as purchased unless otherwise stated. The  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_8$  and  $\text{W}(\text{CO})_6$  were purchased from Strem Chemical Co. and the  $\text{Fe}(\text{CO})_5$  and  $\text{KOCH}_3$  from Alfa-Thiokol. All solvents were dried prior to use by distillation over  $\text{CaH}_2$  or in the case of alcohols over magnesium metal. The carbon monoxide grade C. P. 99.5% was purchased from Matheson and the hydrogen and carbon dioxide were purchased from Strate Welding. The carbon dioxide was of "bone dry" grade. Even though the presence of water could not be identified by infrared spectroscopy or gas chromatography, the carbon dioxide was dried by passing the gas through two 2 1/2" x 2' glass columns of 3A molecular sieves prior to use. A trace amount of carbon monoxide was observed by gas chromatography to be present in the carbon dioxide.

### Instrumentation

All air sensitive manipulations were performed in a Vacuum Atmosphere Co. model HE-43-2 inert atmosphere box or in an Aldrich inert atmosphere glovebag. All experiments were performed under either a nitrogen, carbon dioxide or carbon monoxide atmosphere. GC analyses were performed on a model 3700 FID Varian gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a 1/8" x 8' stainless steel 5% diethylene glycol adipate on chromosorb P (80/100) column. GC mass spectrometry was performed by Dr. R. King of the Microanalytical Laboratory, University of Florida, Gainesville, Florida. Samples were run on an AEI MS30 mass spectrometer with a KOITOS DS55 data station. The system was equipped with a PYE Unicam 104 gas chromatograph containing a 1/4" x 5' glass 10% diethylene glycol succinate on chromosorb W-AW (80-100) column. Infrared spectra were obtained on either a Nicolet 7199/170SX FT spectrometer or a Nicolet 5DXB FTIR spectrometer. All solution samples were run using 0.025 mL path length NaCl cells. All solid samples were run as mulls using KBr salt plates. All catalytic or high pressure experiments were performed using a 250 mL Parr pressure bottle equipped with a brass Swagelok pressure head.<sup>66</sup> This reactor system could withstand a maximum of 120 psig of pressure.

### Preparation of Potassium Tetracarbonylcobaltate(1-)

The  $\text{KCo(CO)}_4$  salt was prepared by a procedure similar to that reported by Edgell and Barbetta.<sup>67</sup> Inside an inert

atmosphere box, a total of 4.80 g of powdered KOH was added to 50 mL of tetrahydrofuran. Another solution containing 2.0 g of  $\text{Co}_2(\text{CO})_8$  in 20 mL of tetrahydrofuran was prepared. The solutions were mixed together and stirred. After one hour the red-black solution had turned yellow in color and a pink precipitate had formed. The solution, which contained the  $\text{KCo}(\text{CO})_4$ , was filtered away from the precipitate and used in the carbon dioxide experiments. The  $\text{KCo}(\text{CO})_4$  salt was characterized by infrared spectroscopy as shown in Table 2-6.

#### Preparation of Potassium Tetracarbonylferrate(2-)

The  $\text{K}_2\text{Fe}(\text{CO})_4$  salt was prepared by a procedure similar to that reported by Krumholz and Stettiner.<sup>68</sup> A solution of 0.80 g of KOH and 1.25 g of  $\text{Ba}(\text{OH})_2$  in 50 mL of distilled water was degassed with  $\text{N}_2$  for one hour. Then 1.0 mL of  $\text{Fe}(\text{CO})_5$  was syringed into the stirred solution. After one hour the yellow solution had turned orange in color. After an additional two hours the solution was red in color and a white precipitate had formed. Inside a glovebag, the red solution containing the  $\text{K}_2\text{Fe}(\text{CO})_4$  was filtered away from the precipitate. The red solution was placed onto a vacuum line and the solvent evaporated to yield a brown solid. The solid was dried and stored under vacuum until used in the carbon dioxide experiments. The iron salt was characterized by infrared spectroscopy as shown in Table 2-6.

Preparation of Sodium Pentacarbonylmanganate(1-) and Sodium Pentacarbonylrhenate(1-)

The  $\text{NaM}(\text{CO})_5$  salt ( $\text{M} = \text{Mn}, \text{Re}$ ) was prepared by a procedure similar to that reported by King and Eisch.<sup>69</sup> Seven milliliters of mercury was added to a nitrogen purged reaction flask. A total of 0.50 g of sodium metal was slowly added to the stirred mercury. Inside an inert nitrogen glovebag a solution containing either 2.98 g of  $\text{Mn}_2(\text{CO})_{10}$  or 1.00 g  $\text{Re}_2(\text{CO})_{10}$  in 50 mL of acetonitrile or tetrahydrofuran was prepared. The solution was quickly added to the stirred amalgam. After 2 1/2 hours the stirring was stopped and the excess sodium-mercury amalgam was removed from the reaction flask. The resulting army green  $\text{NaMn}(\text{CO})_5$  and orange  $\text{NaRe}(\text{CO})_5$  solutions were used in the carbon dioxide experiments. The manganese and rhenium salts were characterized in solution by infrared spectroscopy as shown in Table 2-6.

Preparation of Potassium  $\mu$ -Hydridobis(pentacarbonyl-tungsten(O))

The  $\text{KH}[\text{W}(\text{CO})_5]_2$  was prepared by a procedure similar to that reported by Grillone and Kedzia.<sup>70</sup> Inside a glovebag a solution containing 5.63 g of  $\text{W}(\text{CO})_6$  and 6.3 g KOH in 7.5 mL water, 30 mL methanol and 70 mL tetrahydrofuran was prepared. The solution was heated to 45°C for five hours and then continued stirring at room temperature for an additional 14 hours. The reaction solution was filtered and the resulting filtrate placed onto a vacuum line. The solvent was removed to yield a yellow paste. A total of 82 mL of



Table 2-6. Characterization of Prepared Transition Metal Carbonyl Anions by Infrared Spectroscopy

Compound	Infrared Data (cm <sup>-1</sup> )	Environment	Reference
KCo(CO) <sub>4</sub>	1890(vs)	THF	a(I)
KCo(CO) <sub>4</sub>	1890(vs), 1857(w)	THF	71
K[HF <sub>2</sub> Fe(CO) <sub>4</sub> ] <sup>-</sup>	1915(m), 1887(vs)	acetonitrile	a(II)
HF <sub>2</sub> Fe(CO) <sub>4</sub> <sup>-</sup>	2015(w), 1937(sh), 1897(vs)	water	72
Fe(CO) <sub>4</sub> <sup>=</sup>	1786(vs)	water	72
H <sub>2</sub> Fe(CO) <sub>4</sub>	2121(w), 2111(vw), 2053(m), 2042(s), 2029(vw), 2010(m)	hexane	73
Fe(CO) <sub>5</sub>	2020(vs)	neat	74
NaMn(CO) <sub>5</sub>	1910(vs), 1860(vs)	acetonitrile	a (Fig. 2-5)
KMn(CO) <sub>5</sub>	1896(s), 1862(s), 1830(m)	THF	71
Mn <sub>2</sub> (CO) <sub>10</sub>	2045(s), 2009(vs), 1978(s)	THF	a (III)
HMn(CO) <sub>5</sub>	2117, 2043, 2015(vs), 2008(vs), 1981(vs), 1966	cyclohexane	75
NaRe(CO) <sub>5</sub>	1900(m), 1860(m)	THF	a (IV)
KRe(CO) <sub>5</sub>	1911(s), 1864(s), 1835(sh)	THF	71
Re <sub>2</sub> (CO) <sub>10</sub>	2008(ms), 1972(s)	THF	a (IV)
HRe(CO) <sub>5</sub>	2131, 2123, 2053, 2042, 2015(vs), 2005(vs), 1982(vs)	cyclohexane	75

a = this work; (I-IV) location of spectrum in appendix A;  
 vs = very strong; s = strong; ms = medium strong; m = medium;  
 w = weak; vw = very weak; sh = shoulder.

water was added and the mixture stirred for 24 hours at room temperature followed by 23 additional hours at 0°C in an ice bath. The mixture was filtered to obtain white crystals which were dried and stored under vacuum until used in the carbon dioxide experiments.

#### Preparation of a Mixture of Rhenium Carbonyl Hydrides

The mixture of rhenium carbonyl hydrides was prepared by a procedure similar to that reported for the formation of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ .<sup>76</sup> A solution containing 2.0 g of  $\text{Re}_2(\text{CO})_{10}$  and 1.6 g of  $\text{NaBH}_4$  in 50 mL of tetrahydrofuran was refluxed for 4 hours. The solution went through a sequence of color changes from yellow to orange and finally to red after 4 hours at reflux temperature. The solution was decanted away from the  $\text{NaBH}_4$  and the solvent evaporated. The resulting solid compound was dried under vacuum for several days. A solution containing 80 mL of cyclohexane and 10 mL of  $\text{H}_3\text{PO}_4$  (deaerated and dried by adding several drops of Na-Hg amalgam) was added to the solid compound in the reaction flask. After 6 hours at reflux temperature, the solution was extracted several times with hot cyclohexane. Cooling the cyclohexane solution did not precipitate the desired product as reported. Thus the solvent was evaporated to yield a brown solid which was characterized by infrared spectroscopy to be a mixture of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  and  $\text{Re}_2(\text{CO})_{10}$ .

#### Reaction of the Transition Metal Carbonyl Salts with Carbon Dioxide

Acetonitrile or tetrahydrofuran solutions of the transition metal carbonyl salts were reacted with carbon

dioxide at atmospheric pressure by bubbling the gas through the solution. Higher pressure experiments were performed by using a Parr pressure bottle system<sup>66</sup> containing the solution of the transition metal carbonyl salt and carbon dioxide. The resulting color changes for these reactions are summarized in Table 2-7. The reaction products were examined by infrared spectroscopy.

Table 2-7. Color Changes for Reactions Between Carbon Dioxide and Transition Metal Carbonyl Anions

<u>Anion</u>	<u>Initial Solution Color</u>	$\xrightarrow{\text{CO}_2}$	<u>Final Solution Color</u>
KCo(CO) <sub>4</sub>	Yellow		Yellow
K <sub>2</sub> Fe(CO) <sub>4</sub>	Pink-red		Orange
NaMn(CO) <sub>5</sub>	Army green		Orange-red
NaRe(CO) <sub>5</sub>	Orange		Yellow-green

Reaction of Carbon Dioxide and Hydrogen with Transition Metal Hydrides in Alcohol Solvents

A Parr pressure bottle reactor system containing a solution of  $1.5 \times 10^{-4}$  moles of the catalyst in 20 mL of methanol was charged with either carbon dioxide, hydrogen, carbon monoxide or some mixture of the three gases in equal parts while maintaining the total pressure at 20 psig. The solution was stirred and allowed to react within a temperature range of 125-150°C. The gaseous reaction

products were characterized by gas chromatography, while the liquid reaction mixture was monitored by both gas chromatography and infrared spectroscopy.

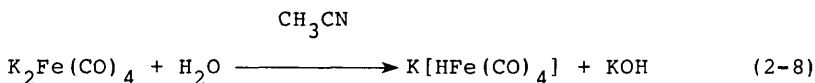
### Results and Discussion

#### The Binding of Carbon Dioxide by Transition Metal Carbonyl Anions

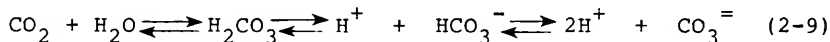
Following the increasing trend in the nucleophilicity (Table 2-3) of the transition metal carbonyl anions, the alkali metal salt of each anion was prepared and reacted with "bone dry" carbon dioxide. The reaction products were characterized by infrared spectroscopy as summarized in Table 2-8. The reaction of carbon dioxide with  $K[Co(CO)_4]$  in tetrahydrofuran at atmospheric and elevated pressures (<70 psig) substantiated the literature reports of the occurrence of no reaction.<sup>50</sup>

Characterization of the iron salt in acetonitrile by infrared spectroscopy (Table 2-6) determined the complex to be  $K[HFe(CO)_4]$  instead of  $K_2Fe(CO)_4$ . It is a common procedure to form hydridometal complexes from the protonation of metal complex anions with water as reported for several phosphine substituted metal carbonyl anions.<sup>77,78</sup> Although unsubstituted metal carbonyl anions usually require acidification to form a hydrido complex, it is reasonable to assume that the trace quantities of water observed by infrared spectroscopy to be present may be a strong enough acid in acetonitrile to partially protonate  $K_2Fe(CO)_4$  to form  $K[HFe(CO)_4]$ . The presence of this trace

quantity of water is a result of the synthesis of the iron salt in a water solution, as well as the difficulty in drying acetonitrile. Upon reaction of this acetonitrile solution of  $\text{K}[\text{HFe}(\text{CO})_4]$  with "bone-dry" carbon dioxide for several hours at atmospheric pressure, several infrared absorptions (Table 2-8) indicative of a reduced carbon dioxide species were observed. These new infrared absorptions correspond very well with the formation of a small quantity of potassium bicarbonate.<sup>79</sup> During the protonation of  $\text{K}_2\text{Fe}(\text{CO})_4$  by trace quantities of water, the formation of potassium hydroxide is inevitable as shown in Equation 2-8. Carbon dioxide can be neutralized by this potassium hydroxide to form potassium bicarbonate. Carbon



dioxide also can be hydrated in the presence of water to form carbonic acid which can dissociate into bicarbonate and carbonate as shown in Equation 2-9. It previously has been suggested by the interpretation of solution infrared data that the reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  with carbon dioxide yields iron pentacarbonyl and sodium carbonate.<sup>48</sup> The preliminary



nature of these reported results has precluded any direct

Table 2-8. A Summary of Infrared Data Obtained for Reactions Between Carbon Dioxide and the Transition Metal Carbonyl Anions

Compound + CO <sub>2</sub>	Infrared Data (cm <sup>-1</sup> )	Assignment	Environment
KCo(CO) <sub>4</sub>	1890 (vs)	KCo(CO) <sub>4</sub> (V)	THF
K[HFe(CO) <sub>4</sub> ]	1915 (m), 1887 (vs) 3600 (mw), 3190 (mw), 1629 (m), 1345 (w), 699 (m)	K[HFe(CO) <sub>4</sub> ] (VI) KHCO <sub>3</sub> (VI)	CH <sub>3</sub> CN CH <sub>3</sub> CN
NaMn(CO) <sub>5</sub>	2044 (m), 2015 (s), 1985 (s) 1910 (vs), 1860 (vs) 1656 (s), 1623 (vs), 1047 (m), 1033 (m), 996 (s), 833 (s), 703 (s)	Mn <sub>2</sub> (CO) <sub>10</sub> (Fig.2-5) NaMn(CO) <sub>5</sub> (Fig.2-5) NaHCO <sub>3</sub> (Fig.2-4)	CH <sub>3</sub> CN CH <sub>3</sub> CN nujol
NaMn(CO) <sub>5</sub> + Mn <sub>2</sub> (CO) <sub>10</sub>	2045 (m), 2010 (s), 1975 (s) 1895 (vs), 1855 (vs) 3460 (w), 2030 (s), 1935 (w), 1667 (w)	Mn <sub>2</sub> (CO) <sub>10</sub> (Fig.2-6) NaMn(CO) <sub>5</sub> (Fig.2-6) "not identified", (Fig.2-6)	THF THF THF
NaRe(CO) <sub>5</sub> + Re <sub>2</sub> (CO) <sub>10</sub>	1985 (s) 1880 (s)	Re <sub>2</sub> (CO) <sub>10</sub> (VII) NaRe(CO) <sub>5</sub> (VII)	THF THF

(V-VII) = location of spectrum in appendix A; vs = very strong; s = strong; m = medium; mw = medium weak; w = weak.

comparisons of the reaction conditions and infrared data with the corresponding conditions and data observed for the reaction of  $\text{K}[\text{HFe}(\text{CO})_4]$  with carbon dioxide. The determination through infrared spectroscopy (Table 2-8) that  $\text{K}[\text{HFe}(\text{CO})_4]$  was the only iron species present after completion of the reaction supports the formation of potassium bicarbonate from the reaction of carbon dioxide with a reaction contaminant, such as water or potassium hydroxide.

Characterization of an acetonitrile solution of  $\text{NaMn}(\text{CO})_5$  (nucleophilicity = 77)<sup>53</sup> by infrared spectroscopy (Table 2-6) showed the absence of  $\text{Mn}_2(\text{CO})_{10}$ , as well as the absence of any residual water. This solution was reacted with "dry" carbon dioxide at atmospheric pressure to yield a solution color change coinciding with the precipitation of a solid. This solid was identified by infrared spectroscopy to consist of primarily sodium bicarbonate with possibly the presence of a trace amount of sodium carbonate as shown in Figure 2-4. The reaction between carbon dioxide and  $\text{NaMn}(\text{CO})_5$  in tetrahydrofuran previously has been reported to yield sodium bicarbonate and an unidentified manganese carbonyl complex.<sup>50</sup> Interpretation of the infrared spectrum of the reaction solution, which is shown in Figure 2-5, suggests that another manganese carbonyl complex is present along with  $\text{NaMn}(\text{CO})_5$ . The infrared absorptions (Table 2-8) assigned to this manganese carbonyl complex correspond to those of  $\text{Mn}_2(\text{CO})_{10}$ . An increase in the quantity of

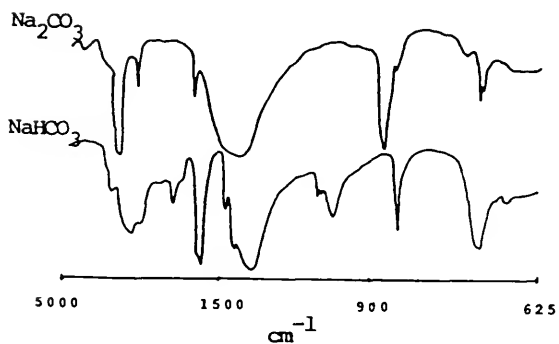
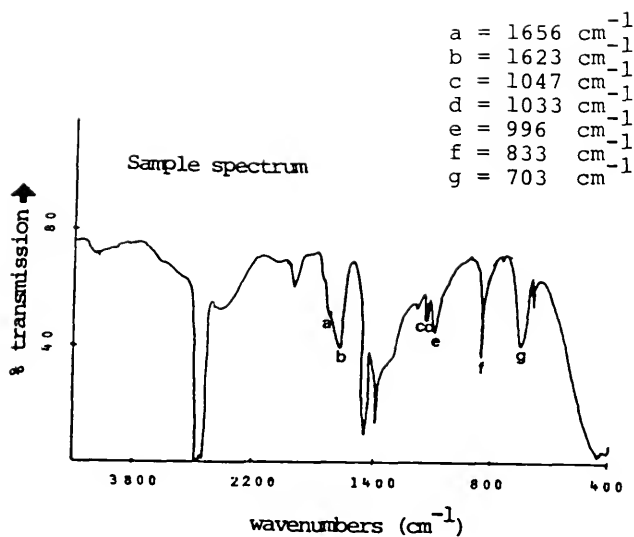


Figure 2-4. Infrared Spectrum of Precipitate  
Obtained from Reaction of Carbon  
Dioxide and  $\text{NaMn}(\text{CO})_5$



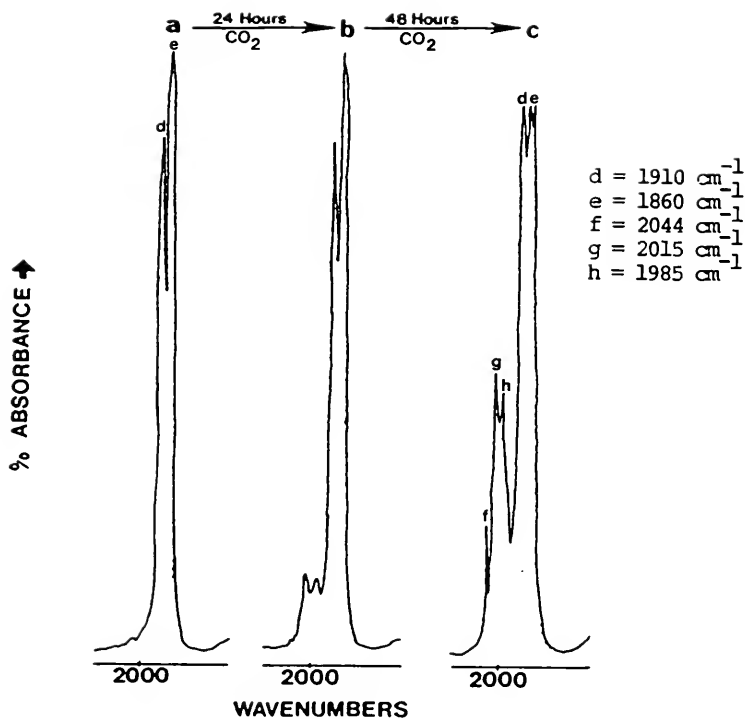


Figure 2-5. Solution Infrared Spectrum of the Carbonyl Region for the Reaction between Carbon Dioxide and  $NaMn(CO)_5$  in Acetonitrile

$\text{Mn}_2(\text{CO})_{10}$  present in the reaction solution was observed in these infrared data to coincide with an increase in reaction time. The reaction of  $\text{NaMn}(\text{CO})_5$  and carbon dioxide in tetrahydrofuran instead of acetonitrile produced similar results. In this case, the presence of a third unidentified manganese complex along with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{NaMn}(\text{CO})_5$  was observed by infrared spectroscopy as shown in Figure 2-6. The infrared absorptions at 2030 and 1935  $\text{cm}^{-1}$  assigned to this unidentified complex were observed to disappear upon the replacement of the carbon dioxide atmosphere with nitrogen. The weak  $\nu_{\text{OH}}$  and  $\nu_{\text{CO}_2}$  absorptions that were observed could be due to either a small quantity of solubilized bicarbonate or to a bound formato, bicarbonato, or metallocarboxylic acid complex of manganese. The identification of a metallocarboxylic acid derivative,  $[(\text{OC})_3\text{M}(\text{CO}_2\text{Na})]_2$  ( $\text{M} = \text{Mn}, \text{Re}$ ) from solution infrared data has been reported for the reaction of carbon dioxide with  $\text{NaM}(\text{CO})_5$  ( $\text{M} = \text{Mn}, \text{Re}$ ).<sup>51</sup> Attempts to isolate a bound carbon dioxide complex have been unsuccessful.

The interaction of carbon dioxide with  $\text{NaMn}(\text{CO})_5$  could proceed through a variety of different pathways. First, it is possible that carbon dioxide directly interacts with  $\text{NaMn}(\text{CO})_5$  forming a metallocarboxylic acid derivative as previously suggested.<sup>51</sup> The observed reaction also could proceed through the disproportionation of carbon dioxide into carbon monoxide and carbonate as shown in Equation 2-10. It is possible that the insertion of carbon dioxide

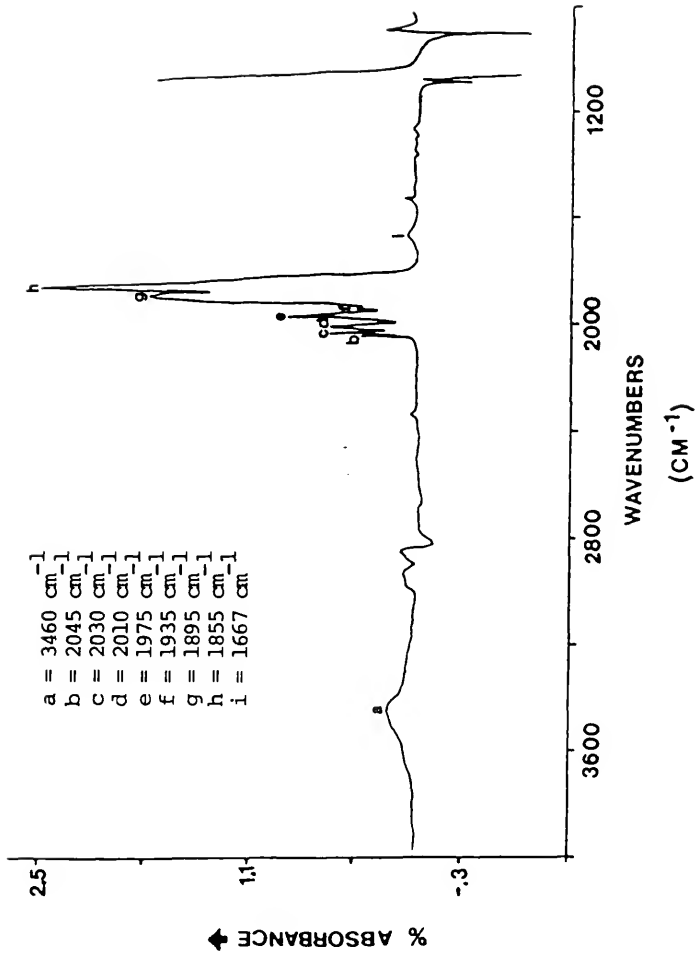
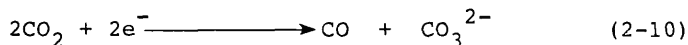


Figure 2-6. Solvent Subtracted Infrared Spectrum for the Reaction between Carbon Dioxide and  $\text{NaMn}(\text{CO})_5$  in Tetrahydrofuran

into the sodium-manganese bond could form an intermediate similar to that isolated for  $\text{IrCl}(\text{C}_2\text{O}_4)(\text{PMe}_3)_3 \cdot 0.5 \cdot \text{C}_6\text{H}_6$ .<sup>35</sup> The disproportionation of this intermediate into carbonate



and carbonyl complexes could explain the observed infrared data. A third alternate way in which a carbonate or bicarbonate species could be formed is by the interaction of carbon dioxide with water as shown in Equation 2-9.

However, the absence of any observable O-H absorptions in the infrared data obtained for the starting solution (Table 2-6) suggests that water is initially not present in the reaction. It is possible that the reverse of the water-gas shift reaction as shown in Equation 2-6 could produce the water necessary to initiate the formation of bicarbonate and carbonate species. Hydrogen was found to be present in the reaction as a low level impurity arising from the "dry" carbon dioxide feed gas. It is impossible to ascertain from the available data which of these mechanisms is predominantly responsible for the observed results.

Reaction between carbon dioxide and a mixture of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{NaRe}(\text{CO})_5$  (nucleophilicity = 25,000)<sup>53</sup> in tetrahydrofuran could not be detected by infrared spectroscopy. Infrared spectroscopy has been inconclusive in ascertaining the existence of any rhenium complex besides  $\text{Re}_2(\text{CO})_{10}$  or  $\text{NaRe}(\text{CO})_5$ . Attempts to stabilize or isolate

any reduced carbon dioxide species has been unsuccessful. Even though the results concerning the reaction between carbon dioxide and  $\text{NaRe}(\text{CO})_5$  have been inconclusive, the formation of sodium carbonate and an unidentified metal carbonyl species has been reported<sup>50</sup> for the reaction of carbon dioxide with the more nucleophilic complex,  $\text{Na}[\text{CpNi}(\text{CO})]$  (nucleophilicity = 7,500,000)<sup>53</sup>.

#### Formation of Alkyl Formates at Low Pressures and Temperatures

The activation of hydrogen by a transition metal carbonyl complex is necessary to effectively utilize the corresponding transition metal carbonyl hydride as a catalyst for the reduction of carbon dioxide. The activation of hydrogen by  $\text{Mn}_2(\text{CO})_{10}$  has been reported to occur only under extreme conditions of pressure and temperature<sup>80</sup>. On the other hand,  $\text{Re}_2(\text{CO})_{10}$  has been reported to activate hydrogen at atmospheric pressure under mild temperature conditions to form a mixture of  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $\text{H}_4\text{Re}_4(\text{CO})_{12}$ .<sup>81</sup> Low temperatures and pressures have been reported to be effective for the activation of hydrogen by  $\text{Ru}_3(\text{CO})_{12}$ <sup>81</sup> and neutral group 6B metal complexes,<sup>49</sup> such as  $\text{W}[\text{P}(\text{OCH}_3)_3]_5\text{H}_2$ . However, the current method for the formation of group 6B metal carbonyl hydrides is the reduction of the hexacarbonyl metal complex by either  $\text{NaBH}_4$ <sup>82</sup> or two equivalents of  $\text{KOH}$  in aprotic solvents.<sup>57</sup> Dodecacarbonyl dirhenium was tested as a catalyst for the conversion of carbon dioxide and hydrogen to methyl formate

in methanol at mild temperatures (125-150°C) and pressures (20 psig). It should be noted that the major difference between the reactions conducted in this work and those previously reported<sup>59-61</sup> in the literature is the utilization of substantially lower pressures in the present work. The reaction products were monitored by gas chromatography and infrared spectroscopy.

The quantitative results of the experiments conducted are summarized in Table 2-9. The formation of methyl formate was observed by gas chromatography and identified by GC/MS as shown in Figure 2-7. Since only a trace amount of methyl formate was discovered in the reaction of  $\text{Re}_2(\text{CO})_{10}$  with carbon dioxide and hydrogen (run 1), no quantitative data were obtained. A control reaction (run 2) involving only methanol, carbon dioxide and hydrogen showed no activity for the formation of methyl formate. Analysis by GC/MS of the reaction mixture (run 1) identified the existence of several additional low molecular weight products, such as dimethyl ether, dimethoxymethane and hexane. The observed mass spectra of these compounds are shown in Figures 2-8, 2-9 and 2-10. Gas chromatography has been used to obtain quantitative data for these compounds, as well as discover the presence of methane and an unidentified substituent at 1.21 minutes as shown in Figure 2-11. Trace amounts of dimethyl ether and dimethoxymethane were observed by gas chromatography to be the only products formed in the control reaction (run 2). The hexane observed

Table 2-9. A Summary of the Quantitative Data  
Obtained for the Reaction Products  
by Gas Chromatography

Run Number	Reaction Time (Hrs.)	Reaction in Methanol <sup>a</sup>	$(CH_3)_2O$ moles $\times 10^{-6}$	$H_2C(OCH_3)_2$ moles $\times 10^{-9}$	$HCO_2CH_3$ moles $\times 10^{-11}$
1	24	$Re_2(CO)_{10}$ + $CO_2$ + $H_2$	15	14	-
-	48		61	41	weak trace
2	48	$CO_2$ + $H_2$	3.2	2.8	None
3	48	$3Re_2(CO)_{10}$ + $CO_2$ + $H_2$	65	33	weak trace
4	48	$Re_2(CO)_{10}$ + CO	28	130	Trace
5	160	$Re_2(CO)_{10}$ + CO + $H_2$	160	8.0	4.0
6	48	$Re_2(CO)_{10}$ + CO + $KOCH_3$	11	420	None
7	48	$Re_2(CO)_{10}$ + CO + $H_2$ + $KOCH_3$	12	170	None
8	48	$KOCH_3$ + CO	160	510	weak trace
9	48	$H_xRe_y(CO)_z$ + CO	95	10	1.5
10	48	$KH[W(CO)_5]_2$ + CO	14	24	Trace
11	48	$[H_2Re(CO)_4]^-$ + CO +	15	230	0.2
-	140	$[Re_2(CO)_6(\nu-OCH_3)_3]^-$	19	480	0.6

<sup>a</sup> = In all reactions the catalyst concentration was  $7.5 \times 10^{-3}$  moles/liter.

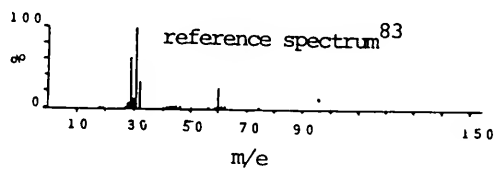
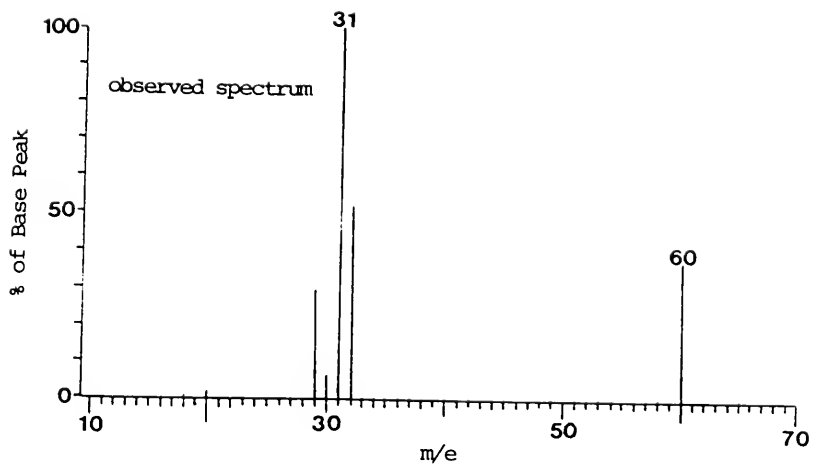


Figure 2-7. Mass Intensity Report for Methyl Formate



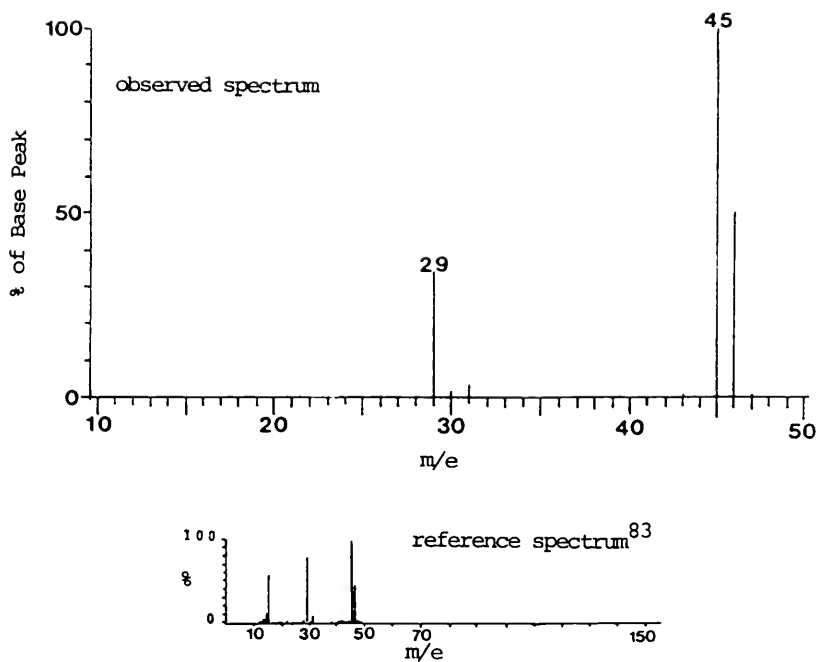


Figure 2-8. Mass Intensity Report for Dimethyl Ether

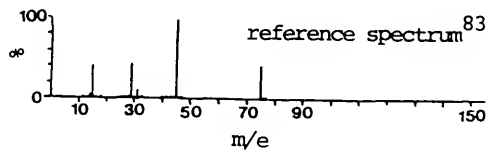
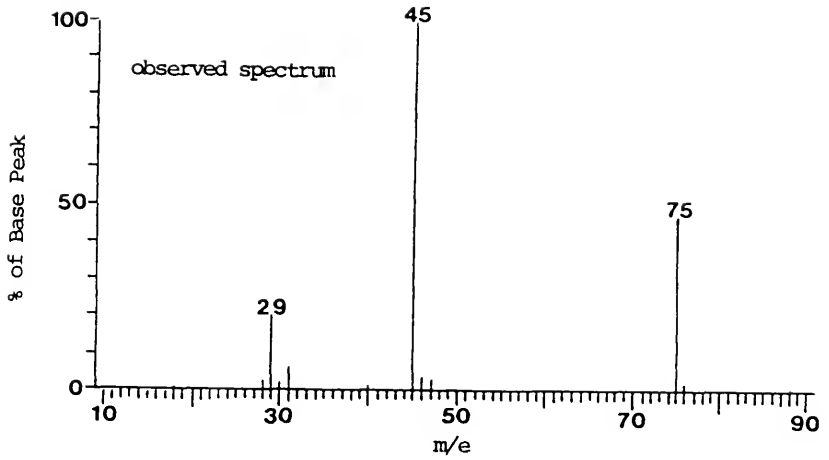


Figure 2-9. Mass Intensity Report for Dimethoxymethane

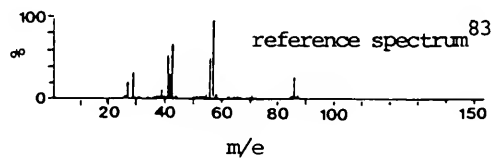
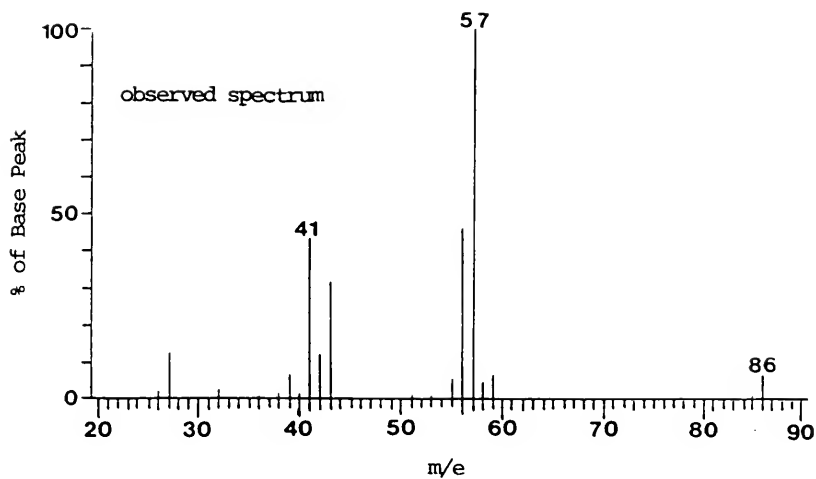
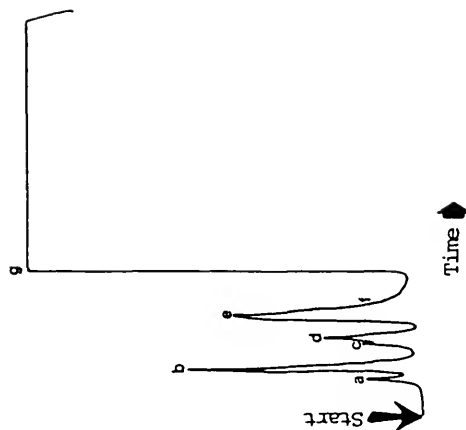


Figure 2-10. Mass Intensity Report for Hexane



- a = 0.56 minutes - methane
- b = 0.77 minutes - dimethyl ether
- c = 1.21 minutes - unidentified
- d = 1.31 minutes - hexane
- e = 1.72 minutes - dimethoxymethane
- f = 1.95 minutes - methyl formate  
(usually observed only in liquid sample)
- g = 2.50 minutes - methanol

Figure 2-11. Gas Chromatogram of Gas Sample Taken During Reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{CO}_2 + \text{H}_2$  in Methanol

in the reaction mixture (run 1) is an impurity that arises from the use of hexane solvent in the commercial recrystallization of  $\text{Re}_2(\text{CO})_{10}$ .<sup>84</sup> Since bulk grade hexane is used, the unidentified peak at 1.21 minutes can be assigned as another hydrocarbon impurity. This is supported by the observed proportional increase in this peak at 1.21 minutes along with the hexane peak as the quantity of  $\text{Re}_2(\text{CO})_{10}$  used in the reaction is increased. Furthermore, both these peaks remain constant throughout the reaction period. The dimethyl ether and the dimethoxymethane that is observed can be considered as reaction products since they increase in concentration as the reaction time progresses (run 1). It also is observed that the  $\text{Re}_2(\text{CO})_{10}$  concentration has no effect upon the quantity of dimethyl ether or dimethoxymethane produced during the reaction (run 3).

It is possible to speculate that methyl formate in this reaction could be produced through a mechanism similar to that previously described<sup>49</sup> in Figure 2-2. Recently, the formation and characterization by x-ray crystallography of a rhenium carbonyl metallocarboxylic acid complex,  $\text{Re}_3(\text{CO})_{14}\text{COOH}$ , was reported.<sup>85</sup> This metallocarboxylic acid complex of rhenium was formed as a minor product in the photolysis of  $\text{Re}_2(\text{CO})_{10}$  in the presence of nitric oxide. It is possible that an intermediate such as this could eliminate formic acid within a catalytic cycle. The interaction of this formic acid with methanol would yield

the observed methyl formate. The infrared data obtained for these carbon dioxide reactions are summarized in Table 2-10. The presence of  $\text{Re}_2(\text{CO})_{10}$  and other rhenium carbonyl complexes is suggested by the interpretation of this infrared data (run 1). The presence of  $\text{Re}_2(\text{CO})_{10}$  in solution was confirmed by the infrared characterization of a white solid that precipitated out of solution upon the addition of water. Subtraction of the  $\text{Re}_2(\text{CO})_{10}$  component in the infrared spectrum (run 1) as shown in Figure 2-12 allows for accurate determination of the absorptions which can be assigned to the appearance of new rhenium carbonyl complexes. The major components in this subtracted infrared spectrum have strong absorptions at 2009 and  $1892\text{ cm}^{-1}$ . It was noticed that during the reaction a pink film was observed to form along the glass reactor walls. Partially dissolving this film in carbon tetrachloride gave an infrared spectrum similar to the solution data (run 1) except for the absence of the absorption at  $1892\text{ cm}^{-1}$ . Since  $\text{Re}_2(\text{CO})_{10}$  has been reported<sup>81</sup> to activate hydrogen within the reaction conditions employed, the infrared absorptions observed for this pink film can be assigned to a mixture of  $\text{Re}_2(\text{CO})_{10}$  and a rhenium carbonyl hydride.

Recently it was reported<sup>62</sup> that the reduction of carbon monoxide by tungsten carbonyl hydrides in methanol catalytically produced methyl formate. The moles of methyl formate formed per mole of catalyst used in these experiments were shown to be approximately two orders of

Table 2-10. A Summary of Infrared Data Obtained for the reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{CO}_2$  and  $\text{H}_2$  in Methanol

Run	Reaction or Complex	Infrared Data, ( $\text{cm}^{-1}$ )	Environment	Reference
1	$\text{Re}_2(\text{CO})_{10} + \text{CO}_2 + \text{H}_2$	2072(m), 2045(m), 2031(m), 2011(vs), 1971(m), 1928(m), 1891(s)	methanol	a (VIII)
	Subtract $\text{Re}_2(\text{CO})_{10}$ and $\text{CH}_3\text{OH}$ out of $\text{Re}_2(\text{CO})_{10}$ spectrum	2031(m), 2009(s), 1999(w), 1929(m), 1892(vs)	methanol	a (Fig. 2-12)
	White precipitate upon addition of water	2070(s), 2014(vs), 1976(s)	nujol	a (IX)
	Pink film	2071(m), 2029(w), 2014(vs), 1974(m), 1934(m)	carbon tetrachloride	a (X)
-	$\text{Re}_2(\text{CO})_{10}$	2072(s), 2012(vs), 1971(s)	methanol	a (XI)
-	$\text{HRe}(\text{CO})_5$	2015(vs), 2005(vs), 1982(vs)	cyclohexane	75
-	$\text{H}_3\text{Re}_3(\text{CO})_{12}$	2093(m), 2083(m), 2030(vs), 2018(vw), 2008(s), 1983(m)	cyclohexane	76
-	$\text{H}_4\text{Re}_4(\text{CO})_{12}$	2043(vs), 1988(vs)	cyclohexane	86

a = This work; (VIII-XI) = location of spectrum in appendix A;  
vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

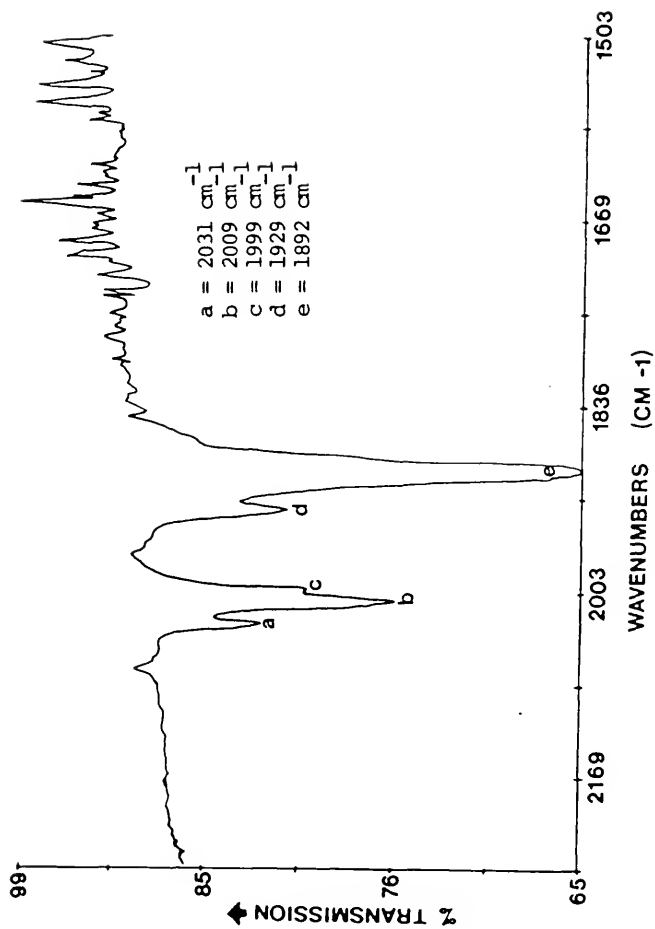


Figure 2-12. Infrared Spectrum of Reaction Products for  $\text{CO}_2/\text{H}_2$  Reaction with  $\text{Re}_2(\text{CO})_{10}$  ( $\text{CH}_3\text{OH}$  and  $\text{Re}_2(\text{CO})_{10}$  have been subtracted out)



magnitude greater than those reported for the corresponding reactions run under carbon dioxide and hydrogen. The small observed activity in the  $\text{Re}_2(\text{CO})_{10}$  reactions run using carbon dioxide and hydrogen can be explained by the reduction of either the metal bound carbonyl ligands or of carbon monoxide produced by the reverse of the water-gas shift reaction as shown in Equation 2-6. This latter case is possible since both  $\text{Re}_2(\text{CO})_{10}$  and  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  have been reported to catalyze the water-gas shift reaction under basic conditions.<sup>87</sup> Although the formation of methyl formate was still too small to quantitate, it was demonstrated by gas chromatography that more methyl formate was formed under a carbon monoxide atmosphere (run 4). The yield of methyl formate was found to increase with the use of a mixture of carbon monoxide and hydrogen over an extended reaction time (run 5). The catalytic ability of the  $\text{Re}_2(\text{CO})_{10}$  system at low pressures will not be discussed since the  $2.6 \times 10^{-7}$  moles of methyl formate formed per mole of  $\text{Re}_2(\text{CO})_{10}$  used is far below one catalyst turnover assuming  $\text{Re}_2(\text{CO})_{10}$  to be the active catalyst.

Infrared spectroscopy was used in an attempt to determine the active species in the  $\text{Re}_2(\text{CO})_{10}$  reaction systems. All infrared data obtained for reactions using carbon monoxide are summarized in Table 2-11. The infrared spectrum of the reaction run under carbon monoxide (run 4) shows the presence of only one absorption at  $1890 \text{ cm}^{-1}$  that cannot be assigned to  $\text{Re}_2(\text{CO})_{10}$ . This suggests that the

Table 2-11. A Summary of Infrared Data Obtained for the Reaction of  $\text{Re}_2(\text{CO})_{10}$  with Carbon Monoxide in Methanol

Run	Reaction or Complex	Infrared Data, $\nu_{\text{CO}}$ , ( $\text{cm}^{-1}$ )	Environment	Reference
4	$\text{Re}_2(\text{CO})_{10} + \text{CO}$	2071(s), 2013(vs), 1971(s), 1891(m)	methanol	a (XII)
6	$\text{Re}_2(\text{CO})_{10} + \text{CO} + \text{KOCH}_3$	2071(m), 2013(s), 1972(m), 1888(s), 1732(w), 1717(w), 1605(vs)	methanol	a (XIII)
7	$\text{Re}_2(\text{CO})_{10} + \text{CO} + \text{H}_2 + \text{KOCH}_3$	2071(w), 2013(s), 2000(s), 1971(w), 1888(vs), 1606(vs)	methanol	a (XIV)
8	$\text{KOCH}_3 + \text{CO}$	1735(m), 1718(m), 1605(vs)	methanol	a (XV)
9	$\text{H}_x\text{Re}_y(\text{CO})_z + \text{CO}$	2072(m), 2031(s), 2010(vs), 1971(m), 1927(vs), 1891(vs)	methanol	a (XVI)
-	Subtract out $\text{Re}_2(\text{CO})_{10}$	2031(s), 2008(s), 1928(vs), 1892(vs)	-	a (Fig. 2-13)
-	$[(\text{CO})_3\text{Re}(\mu\text{-OCH}_3)_3\text{Re}(\text{CO})_3]^-$	1990(s), 1875(vs)	dichloromethane	88
-	$[\text{H}_2\text{Re}(\text{CO})_4]^-$	2020(vw), 1995(w), 1930(vs), 1895(s)	dichloromethane	88
-	$[\text{Re}(\text{CO})_3\text{OCH}_3]_4$	2036, 1935	THF	89
-	$[\text{Re}_3(\mu\text{-H})_3(\mu\text{-OCH}_3)(\text{CO})_{10}]^-$	2096(w), 2020(m), 2000(vs), 1985(sh), 1957(vs), 1935(vs), 1888(s)	dichloromethane	90

a = This work; (XII-XVI) = Location of spectrum in appendix A;  
 vs = very strong; s = strong; sh = shoulder; m = medium; w = weak;  
 vw = very weak.

observed absorptions at 2031 and 1927  $\text{cm}^{-1}$  in reactions run in the presence of hydrogen can be assigned to the formation of a rhenium carbonyl hydride complex such as  $\text{H}_3\text{Re}_3(\text{CO})_{12}$ . Since methyl formate formation was enhanced in the presence of hydrogen over an extended reaction time (run 5), it is proposed that the active species in the reaction is a rhenium carbonyl hydride. This proposal is further supported by the enhanced formation of methyl formate in the reaction of carbon monoxide with a mixture of rhenium carbonyl hydrides (run 9). The resulting infrared spectrum for this reaction, which is shown in Figure 2-13, resembles those obtained for reactions between  $\text{Re}_2(\text{CO})_{10}$  with hydrogen and either carbon dioxide (run 1) or carbon monoxide (run 5).

Recall that in the previously proposed mechanism<sup>62</sup> shown in Figure 2-4 for the carbonylation of methanol to methyl formate by tungsten carbonyl hydrides, the active catalytic species was suggested to be a methoxy tungsten carbonyl complex. Recently the bridging methoxy compound  $[(\text{CO})_3\text{Re}(\mu\text{-OCH}_3)_3\text{Re}(\text{CO})_3][\text{N}(\text{C}_2\text{H}_5)_4]$  was reported to be formed by the addition of methanolic KOH to  $\text{Re}_2(\text{CO})_{10}$ .<sup>88</sup> Along with the hexacarbonyl tri- $\mu$ -methoxydirhenate(1-) the reaction was found to form  $[\text{H}_2\text{Re}(\text{CO})_4]^-$  as a coproduct. The complete conversion of this rhenium hydride to the isolated bridging methoxy compound  $[(\text{CO})_6\text{Re}_2(\mu\text{-OCH}_3)_3]^-$  was observed to occur at elevated temperatures. The formation of other alkoxide rhenium carbonyl complexes, such as

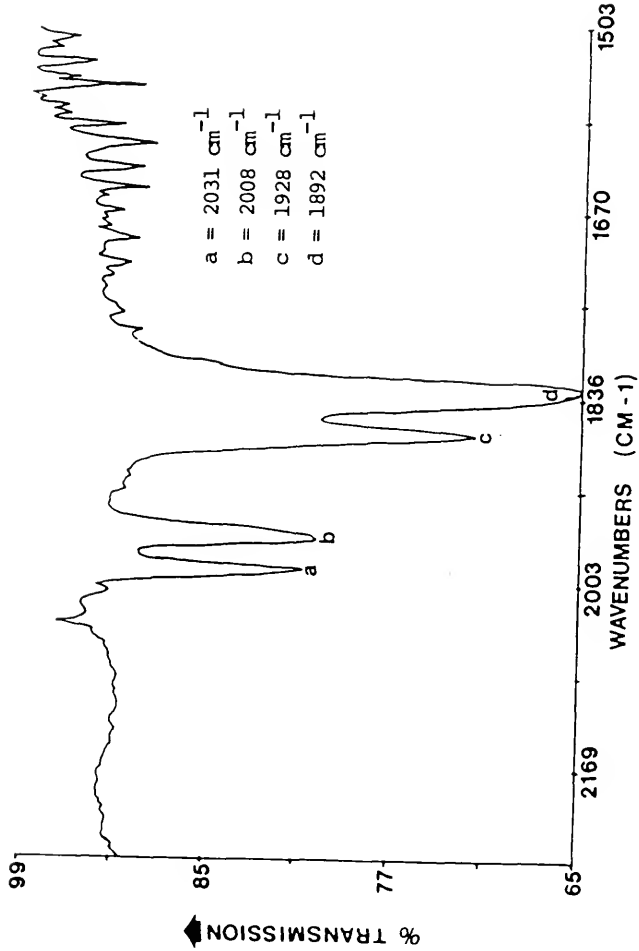


Figure 2-13. Infrared Spectrum of Reaction Products for Rhenium Hydride and CO Reaction with  $\text{Re}_2(\text{CO})_{10}$  and Methanol Subtracted Out

$[\text{Re}(\text{CO})_3\text{OCH}_3]_4$ ,<sup>89</sup>  $[\text{Re}_3(\mu\text{-H})_3(\mu\text{-OCH}_3)(\text{CO})_{10}]^-$ ,<sup>90</sup>  
 $[(\text{CO})_6\text{Re}_2(\mu\text{-OC}_2\text{H}_5)_2(\mu\text{-OCH}_3)]^-$ <sup>91</sup> and  $[\text{Re}_3\text{H}_3(\mu_3\text{-OC}_2\text{H}_5)(\text{CO})_9]^-$ <sup>92</sup> also have been reported. The preparation of these alkoxy rhenium carbonyl hydride complexes was reported<sup>92</sup> to proceed through a reaction of a rhenium carbonyl hydride with the corresponding alcohol. The similarities between the infrared spectra for these complexes and the infrared data obtained for the  $\text{Re}_2(\text{CO})_{10}$  reactions (Table 2-11) suggests that the  $1890\text{ cm}^{-1}$  absorption can be assigned to the formation of a methoxy rhenium carbonyl complex such as  $[(\text{CO})_6\text{Re}_2(\mu\text{-OCH}_3)_3]^-$ . This is further supported in that no new infrared absorptions are observed for the addition of several equivalents of  $\text{KOCH}_3$  to the  $\text{Re}_2(\text{CO})_{10}$  reactions run under either carbon monoxide (run 6) or carbon monoxide and hydrogen (run 7). Since gas chromatography could not identify the formation of any methyl formate in these reactions (runs 6, 7), the methoxy rhenium carbonyl complex is most likely catalytically inactive. The infrared spectrum of the reaction performed under carbon monoxide and hydrogen (run 7) was observed not to exhibit any absorptions that could be assigned to a rhenium carbonyl hydride. This suggests that deactivation of the active rhenium carbonyl hydride results in the formation of an inactive methoxy rhenium carbonyl complex. Attempts to isolate this methoxy rhenium carbonyl complex have been unsuccessful.

A mixture of  $[(\text{CO})_3\text{Re}(\mu\text{-OCH}_3)_3\text{Re}(\text{CO})_3]^-$  and  $\text{H}_2\text{Re}(\text{CO})_4^-$  in methanol was prepared by the previously reported procedure<sup>88</sup> and identified by infrared spectroscopy as shown in Figure 2-14. The formation of methyl formate was observed to occur for the reaction (run 11) of carbon monoxide with this mixture of rhenium complexes. The activity observed for the formation of methyl formate was found to decrease with an increase in reaction time. The resulting solution was observed by infrared spectroscopy to contain only the  $[\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]^-$  complex as shown in Figure 2-14. It is proposed that a mixture of rhenium carbonyl hydrides, such as  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Re}(\text{CO})_4^-$  are the active species responsible for the formation of methyl formate from carbon monoxide and methanol. These hydride species can be converted under the employed reaction conditions to the resulting inactive rhenium alkoxy carbonyl complex  $[\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]^-$ . The only infrared absorption in Figure 2-14 that cannot be assigned to either a rhenium carbonyl hydride or alkoxy complex is the medium strength band at  $1605\text{ cm}^{-1}$ . It has been observed by infrared spectroscopy that a similar absorption results from the addition of  $\text{KOCH}_3$  to methanol (run 8).

At elevated pressures the carbonylation of methanol to methyl formate has been reported to occur using sodium methoxide as catalyst.<sup>93,94</sup> A comparison of the low pressure formation of methyl formate by this reaction (run

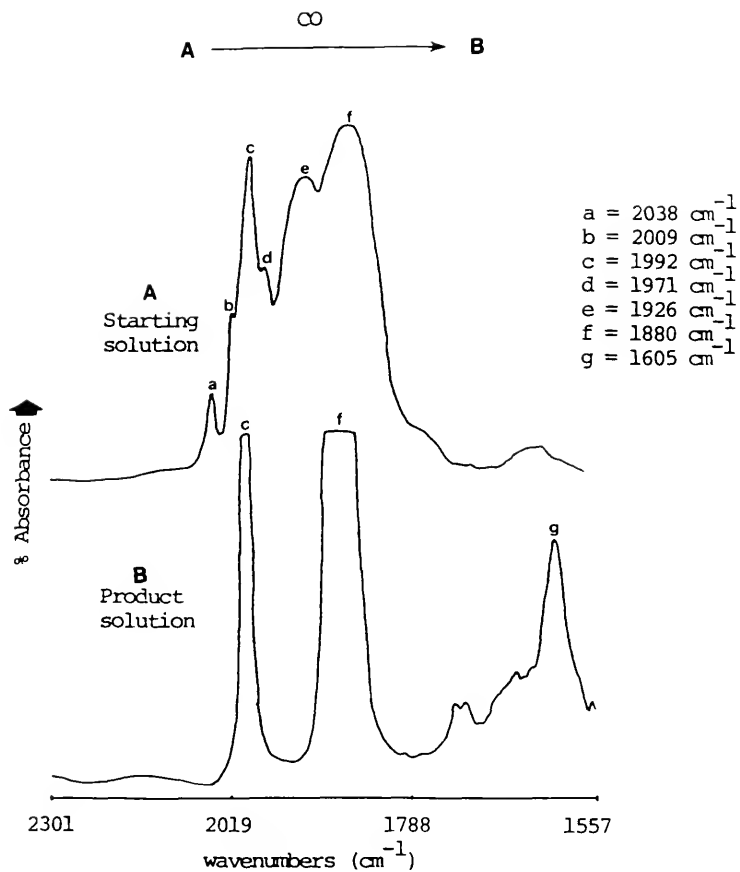
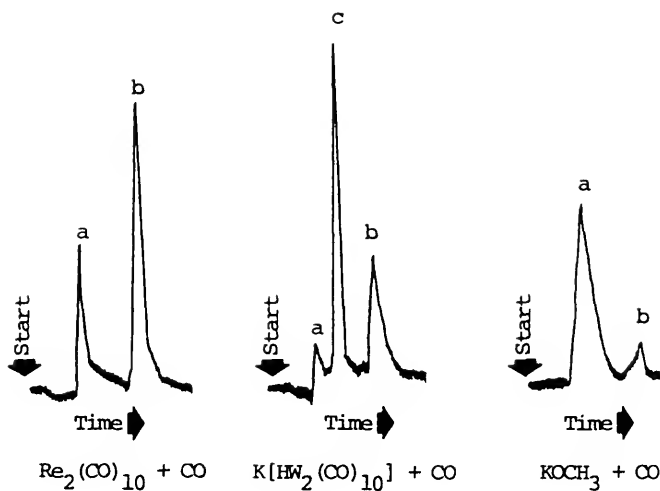


Figure 2-14. Infrared Spectrum Obtained for the Reaction of Carbon Monoxide With a Mixture of  $[\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]^-$  and  $[\text{H}_2\text{Re}(\text{CO})_4]^-$  in Methanol

8) with the  $\text{Re}_2(\text{CO})_{10}$  (run 4) and  $\text{KH}[\text{W}(\text{CO})_5]_2$  (run 10) systems was done. The results as shown in Figure 2-15 indicate that  $\text{Re}_2(\text{CO})_{10} > \text{KH}[\text{W}(\text{CO})_5]_2 > \text{KOCH}_3$  in activity for the carbonylation of methanol at low pressures to form methyl formate. This sequence of activity at low pressures parallels a recent report which indicates that  $\text{KH}[\text{W}(\text{CO})_5]_2$  is more active than  $\text{KOCH}_3$  for the carbonylation of methanol to methyl formate at elevated pressures.<sup>62</sup> An investigation of the activity of the  $\text{Re}_2(\text{CO})_{10}$  system at elevated pressures was not done because of the lack of a high pressure reactor.

The utilization of low pressures in the  $\text{Re}_2(\text{CO})_{10}$  system has allowed the identification of dimethyl ether and dimethoxymethane which may be key intermediates in the formation of methyl formate. A discussion concerning the mechanism for the formation of methyl formate in the  $\text{Re}_2(\text{CO})_{10}/\text{CH}_3\text{OH}/\text{CO}$  system would be speculative and premature at this time. However, it should be noted that formaldehyde has been reported to form dimethoxymethane in methanol<sup>95</sup> and methyl formate in the presence of a nickel catalyst<sup>96</sup>. Although a rhenium carbonyl bound formaldehyde complex has not been observed, both its precursor, a formyl complex, such as  $[\text{Re}_2(\text{CO})_9(\text{CHO})]^-$ <sup>97,98</sup> and its product, an alkoxymethyl complex, such as  $\text{Re}(\text{CO})_5\text{CH}_2\text{OCH}_3$ <sup>99</sup> have been reported. Another way in which dimethoxymethane,<sup>100</sup> dimethyl ether<sup>100</sup> and methyl formate<sup>101,102,103</sup> have been reported to be formed is through the direct oxidation of





a = 0.77 minutes - dimethyl ether

b = 1.95 minutes - methyl formate

c = 1.23 minutes - unidentified

Figure 2-15. A Comparison by Gas Chromatography of Reaction Products in Liquid Samples for Carbon Monoxide Reactions with  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{K}[\text{W}(\text{CO})_5]_2$  and  $\text{KOCH}_3$

methanol over a variety of different catalyst substrates. Carbon-13 carbon monoxide was reacted with  $\text{Re}_2(\text{CO})_{10}$  in methanol to ascertain if the methyl formate was being formed by the carbonylation of methanol or by methanol oxidation. GC/MS results so far have been inconclusive in obtaining the extent of carbon-13 incorporation in dimethyl ether, dimethoxymethane or methyl formate because of the relatively small amounts of products observed. It is proposed that the methyl formate observed in the  $\text{Re}_2(\text{CO})_{10}$  systems is from the carbonylation of methanol as reported for the analogous  $\text{KH}[\text{W}(\text{CO})_5]_2$ <sup>62</sup> and  $\text{KOCH}_3$ <sup>93,94</sup> systems. This proposal is based upon the differences observed in reactions (runs 1-3) performed under carbon dioxide and those reactions (runs 4, 5) performed under carbon monoxide. If the formation of methyl formate was governed by the oxidation of the methanol solvent, there should have been no differences in the observed results.

#### Summary

The main goal of this investigation was to evaluate the feasibility of binding and activating carbon dioxide by transition metal carbonyl complexes. The first study dealt with the interaction of carbon dioxide with a variety of transition metal carbonyl anions that differed in the nucleophilicity of the metal center. Although no reaction with carbon dioxide was observed to occur for  $\text{KCo}(\text{CO})_4$ , the formation of potassium bicarbonate was observed in the  $\text{K}[\text{HFe}(\text{CO})_4]$  system. This result was clouded by the reaction

of carbon dioxide with residual contaminants of water and potassium hydroxide. Interaction of carbon dioxide with  $\text{NaMn(CO)}_5$  was found to form sodium bicarbonate,  $\text{Mn}_2(\text{CO})_{10}$  and an unidentified manganese carbonyl complex. The occurrence of a reaction between carbon dioxide and  $\text{NaRe(CO)}_5$  was not observed. These results suggest that it is possible to bind carbon dioxide to a transition metal carbonyl anion. Although no conclusion concerning the preferred coordination mode of binding can be made, it does seem that the interaction of carbon dioxide with transition metal carbonyl anions is affected by the nucleophilicity of the metal center.

The second study dealt with an investigation of the activity of  $\text{Re}_2(\text{CO})_{10}$  with respect to the reduction of carbon dioxide in methanol to form methyl formate at low pressures. Reactions performed under carbon dioxide and hydrogen produced trace quantities of dimethyl ether, dimethoxymethane and methyl formate as identified by GC and GC/MS. Although these products could be formed directly from carbon dioxide, it is more likely that the reduction of carbon monoxide produced from the reverse of the water-gas shift reaction has occurred. This contention is supported by the increased activity for the formation of all products in reactions run under carbon monoxide.

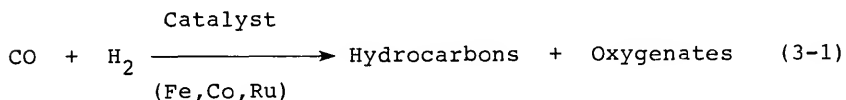
Infrared spectroscopy was used to investigate the active species in these reactions. It has been proposed through an interpretation of this data that the active

species is a mixture of rhenium carbonyl hydrides, such as  $\text{H}_3\text{Re}_3(\text{CO})_{12}$  and  $[\text{H}_2\text{Re}(\text{CO})_4]^-$ . These hydride complexes slowly decompose during the course of the reaction to form the inactive methoxy rhenium carbonyl complex,  $[\text{Re}_2(\text{CO})_6(\mu\text{-OCH}_3)_3]^-$ . Since an accurate measurement of the amount of the active species present during the reaction could not be obtained, a discussion of the  $\text{Re}_2(\text{CO})_{10}$  system's catalytic ability was not undertaken. The formation of dimethoxymethane and dimethyl ether was observed during the course of the reaction. A comparison at low pressures of the  $\text{Re}_2(\text{CO})_{10}$  system with systems, such as  $\text{K}[\text{HW}_2(\text{CO})_{10}]$  and  $\text{KOCH}_3$ , that are known to carbonylate methanol and form methyl formate was done. The results indicate that the activity of  $\text{Re}_2(\text{CO})_{10} > \text{K}[\text{HW}_2(\text{CO})_{10}] > \text{KOCH}_3$  in the carbonylation of methanol to form methyl formate. The possibility of increasing the activity of the  $\text{Re}_2(\text{CO})_{10}$  system at high pressures similar to that previously shown for  $\text{KH}[\text{W}(\text{CO})_5]_2$  and  $\text{KOCH}_3$  may allow for a more thorough investigation of the reaction mechanism.

CHAPTER III  
ACTIVATION OF CARBON MONOXIDE

Background

The conversion of synthesis gas ( $\text{CO} + \text{H}_2$ ) into organic substrates has been an active field of research since the initial work of Sabatier and Sendrens in the early 1900's.<sup>104</sup> Many articles have reviewed various processes that activate carbon monoxide, such as the water-gas shift and Fischer-Tropsch reactions.<sup>105-111</sup> The latter has evolved for the hydrogenation of carbon monoxide and is described in Equation 3-1. The Fischer-Tropsch synthesis<sup>112</sup> usually employs a heterogeneous catalyst consisting of



either Fe, Co or Ru metal. This reaction takes place over a wide range of temperatures and pressures. Moderate temperatures and high pressures seem to favor the formation of oxygenated products while milder pressure conditions increase the ratio of hydrocarbon products.<sup>113</sup> In both cases the ratio of products obtained follows a simple polymerization model (Schulz-Flory distribution) as

described by Equations 3-2 and 3-3.<sup>114-116</sup> In Schulz-Flory

$$W_n = n (1-\alpha)^2 \alpha^{n-1} \quad (3-2)$$

$$Q = \frac{r_p + r_t}{r_t} = \frac{1}{1-\alpha} \quad (3-3)$$

kinetics the weight fraction,  $W_n$ , of carbon number,  $n$ , is related to the probability of chain growth,  $\alpha$ , which is defined in terms of the average degree of polymerization,  $Q$ . The value of  $Q$ , determined from the rate of polymerization,  $r_p$ , and the rate of chain termination,  $r_t$ , is influenced by the characteristics of the metal catalyst and the reaction conditions, such as temperature and pressure. The inherent lack of selectivity as demonstrated by Schulz-Flory kinetics is the major disadvantage to a Fischer-Tropsch type conversion of synthesis gas.

In order to deviate from this Schulz-Flory product distribution, thereby increasing the selectivity of the Fischer-Tropsch synthesis, research efforts have concentrated on new loading techniques<sup>117</sup> and the use of shape selective supports.<sup>118,119</sup> There is considerable evidence that the probability of polymerization in the Fischer-Tropsch synthesis is influenced by the size of the metal crystallites.<sup>116,120,121</sup> A variety of reasons for this particle size effect ranging from differences in the electronic band structure of small particles as compared to

that of the bulk metal to a stronger support interaction and higher degree of unsaturation with small particles have been suggested.<sup>122</sup> The final outcome has been the development of new methods for the preparation of small metal particles, such as the solvated metal atom dispersed catalyst method<sup>123</sup> and the thermal decomposition of metal carbonyl clusters<sup>124</sup> onto inorganic oxide supports. The utilization of these techniques has led in several instances to catalysts that exhibit higher activities and selectivities for synthesis gas conversion to  $C_2 - C_5$  hydrocarbons as compared to conventionally prepared catalysts.<sup>125</sup> These dispersed metal catalysts deposited on high surface area supports are considered a new class of catalysts that lie between the boundaries of traditional heterogeneous and homogeneous catalysts.

As shown in Table 3-1 there are several advantages and disadvantages associated with using either homogeneous or heterogeneous catalysts.<sup>126</sup> The major disadvantage of heterogeneous catalysts besides their non-selective nature has been the lack of physical techniques to adequately characterize these systems. Recent advances in surface techniques, such as ESCA, SEM, XPS, Auger, etc. are beginning to aid in understanding and characterizing these catalyst systems. Homogeneous catalysts, on the other hand, are usually well characterized and reproducible. The major industrial concern for these catalysts is the additional

Table 3-1. A Comparison of the Advantages and Disadvantages of Using Homogeneous and Heterogeneous Catalysts

<u>Advantages</u>	<u>Disadvantages</u>
<u>Homogeneous Catalysts</u>	
1. Relatively resistant to catalyst poisoning	1. Necessary process step for catalyst separation
2. High activity	2. Temperature sensitive
3. No mass-transfer problems	
4. High selectivity	
5. Characterization, reproducible	
<u>Heterogeneous Catalysts</u>	
1. Catalyst easily separated from substrate	1. Sensitive to catalyst poisoning
2. Insensitive to high temperatures	2. Mass transfer problems
	3. Characterization

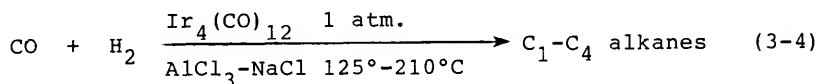
process step that is necessary to separate the reactant/product/catalyst mixture.

Another method to obtain a more selective process focuses around the utilization of homogeneous catalysts for the hydrogenation of carbon monoxide. A vast body of literature has developed for the conversion of synthesis gas to oxygenated products by solubilized catalysts.<sup>127-131</sup> These systems usually operate under extreme pressure conditions (>1000 atm.). Recently there have been several reports of anionic ruthenium carbonyl complexes being



effective in the homogeneous reduction of carbon monoxide to ethylene glycol at moderate temperatures and pressures.<sup>132-133</sup> Moderate temperatures and pressures have also been reported for the conversion of synthesis gas to methanol using a neutral metal complex,  $\text{Ru}(\text{CO})_5$ , as catalyst.<sup>134</sup> The addition of carboxylic acids to this reaction promoted the formation of glycol esters. Most of the homogeneous systems reported have formed oxygenated products from the hydrogenation of carbon monoxide.

Although several non-catalytic systems have been reported that reduce a carbonyl ligand to hydrocarbon products,<sup>135-137</sup> there have been very few reports concerning the homogeneous catalytic reduction of synthesis gas to hydrocarbons. The first report, in 1976, employed selected metal carbonyl cluster catalysts, such as  $\text{Os}_3(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$ .<sup>138</sup> Substitution of several of the carbonyl groups in  $\text{Ir}_4(\text{CO})_{12}$  by triphenylphosphine was found to increase the hydrocarbon production rate. This rate was further enhanced by dissolving the  $\text{Ir}_4(\text{CO})_{12}$  in an  $\text{AlCl}_3$ -NaCl melt solvent as shown in Equation 3-4.<sup>139,140</sup> This reduction of carbon monoxide was done under very mild conditions, 125-210°C and one atmosphere of pressure.



The introduction of metallic aluminum to this system was found to increase the yield of hydrocarbon products.<sup>21</sup> It

was proposed that the addition of this aluminum metal enhanced the formation of  $\text{HALX}_2$  which bifunctionally induced the reduction of carbon monoxide.

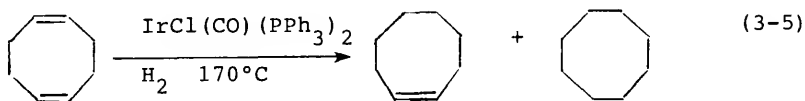
A kinetic investigation of the  $\text{Ir}_4(\text{CO})_{12}$  melt salt system at  $175^\circ\text{C}$  discovered the formation of a sustained low level concentration of methyl chloride which was proposed to be an intermediate in the formation of the hydrocarbon products.<sup>141</sup> This kinetic study proposed that the active catalytic species was a chlorocarbonyl iridium complex, such as  $\text{IrCl}(\text{CO})_3$ . A similar system using  $\text{Os}_3(\text{CO})_{12}$  in a  $\text{BBr}_3$  melt to convert synthesis gas to hydrocarbon products has been reported.<sup>142</sup> In this case, the formation of a low level concentration of methyl bromide was detected. It was suggested that  $\text{Os}_2(\text{CO})_6\text{Br}_4$  was the active catalytic species in the reaction. The most significant contribution of these reports was to demonstrate the importance of a Lewis acid adduct with a metal carbonyl ligand. This bifunctional



activation leads to a weakening of the carbon-oxygen bond which allows the carbonyl group to be reduced under very mild conditions.

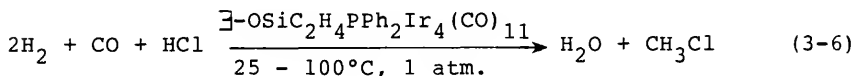
The functionalization of reactive supports with discrete molecular catalyst systems also could utilize this concept of bimetallic synergism by exploiting the support as cocatalyst. These supported catalysts may stabilize and

increase the concentration of the catalytic active species which would allow the reduction of carbon monoxide to occur under milder conditions.<sup>143</sup> The immobilization of homogeneous transition metal catalysts on various polymer supports is currently a very active field in catalysis research. The techniques for the covalent or ionic attachment of discrete metal complexes to various types of supports are well documented.<sup>144,145</sup> These supported catalysts can be considered as "hybrid" catalysts which offer the advantages, such as high activity and selectivity, of homogeneous catalysts as well as the ease of product/catalyst separation associated with heterogeneous catalysts. Several reports have indicated an increase in activity and selectivity using a polymer bound catalyst as compared to its molecular analog.<sup>146</sup> For instance, the polymer bound analog of Vaska's complex,  $(\text{P})-(\text{PPh}_2)_2\text{IrCl}(\text{CO})$ , catalyzes the hydrogenation of 1,5-cyclooctadiene at a faster rate than observed for the homogeneous reaction as shown in Equation 3-5.<sup>147</sup>

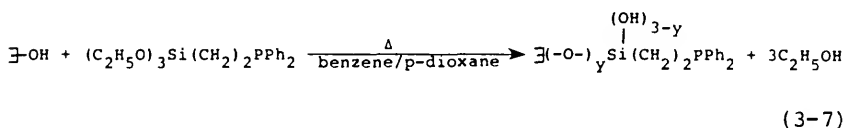


Prior work done concerning the catalytic behavior of supported complexes in Dr. Drago's research group led to the discovery of a unique system for the selective catalytic conversion of synthesis gas and HCl to methyl chloride by a

supported tetrairidium cluster under very mild temperature (25°-100°C) and pressure (1 atm.) conditions<sup>148</sup> as shown in Equation 3-6. The support of choice was an inorganic oxide

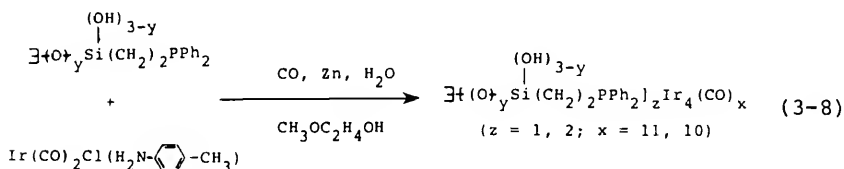


(alumina or silica gel) because of its high thermal stability and the availability of Lewis acid sites to promote a bifunctional interaction with carbon monoxide. The support was functionalized through a condensation reaction involving the hydroxyl groups of the support and the ethoxy substituents of the phosphinated silane linkage,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_2\text{H}_4\text{PPh}_2$  as shown in Equation 3-7.<sup>149</sup> The letter y represents the number of support 3-O-Si bonds between



the support surface and the silane linkage. Evidence indicates that this number is dependent upon the concentration of the organosilane used.<sup>150</sup> The remaining ethoxy groups have been reported to be hydrolyzed by the solvent to yield ethanol and Si-OH functionalities. The tetrairidium carbonyl cluster was immobilized on the support

through covalent attachment to the phosphine of the silane linkage as previously reported.<sup>151,152</sup> The major difficulty in this synthesis, as shown in Equation 3-8, was to maintain



adequate stirring during the reaction. A poorly active catalyst was reported in cases where complete mixing was not obtained. An infrared investigation of the supported tetrairidium cluster, as summarized in Table 3-2, was reported to result in the identification of a mixture of mono-phosphine and di-phosphine substituted clusters,  $\exists\text{-OSi}(\text{CH}_2)_2\text{PPh}_2\text{Ir}_4(\text{CO})_{11}$  and  $\exists\text{-[OSi}(\text{CH}_2)_2\text{PPh}_2]_2\text{Ir}_4(\text{CO})_{10}$ , respectively.

The catalyst was initially tested in a 3:1  $\text{AlCl}_3\text{-NaCl}$  melt salt under similar conditions as reported by Meutterties et al.<sup>140</sup> and Collman et al.<sup>141</sup> for the  $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$  system. A typical catalyst run consisted of using 0.7 g of the supported iridium catalyst, 8 g of  $\text{AlCl}_3$  and 1.8 g of  $\text{NaCl}$  in a glass fixed bed reactor system. The catalyst was exposed to a 3:1 mixture of  $\text{H}_2\text{:CO}$  at  $145^\circ\text{C}$ . The major products were identified by gas chromatography to be methane, ethane, and chloromethane which are similar to those previously reported

Table 3-2. A Summary of the Infrared Data Reported for the Supported Iridium Carbonyl Catalysts

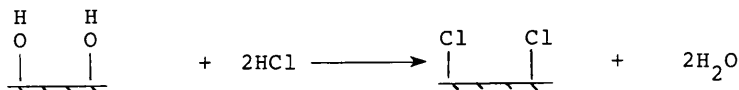
Compound	Infrared Data		Reference
	( $\text{cm}^{-1}$ ), $\nu_{\text{CO}}$	Environment	
$\text{Ir}_4(\text{CO})_{12}\text{PPh}_3$	2088(m), 2056(s), 2020(s), 1887(vw), 1847(m), 1825(m)	dichloromethane	151
$\text{Ir}_4(\text{CO})_{10}(\text{PPh}_3)_2$	2067(m), 2041(s), 2006(s), 1827(m), 1795(m)	dichloromethane	151
$\text{SG} \sim \text{PPh}_2\text{Ir}_4(\text{CO})_{11}$	2090(m), 2061(m), 2023(m), 1890(vw), 1835(m), 1825(m)	wafer	151
$\text{SG}(\sim \text{PPh}_2)_2\text{Ir}_4(\text{CO})_{10}$	2074(s), 2050(vs), 2017(m)	wafer	151
$\text{SG}(\sim \text{PPh}_2)_1,2\text{Ir}_4(\text{CO})_{11,10}$	2092(sh), 2070(sh), 2041(s), 2005(m)	nujol	148
$\text{Al}(\sim \text{PPh}_2)_1,2\text{Ir}_4(\text{CO})_{11,10}$	2114(m), 2060(m), 2004(s)	diffuse reflectance	148
$\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$	2190(s), 2160(vs), 2125(s), 2112(m), 1630(m)	nujol	140
$\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$	2200-2000 (multibonds)	$\text{AlCl}_3\text{-NaCl melt}$	141

SG = silica gel; Al = alumina; m = medium; vw = very weak; s = strong; vs = very strong; sh = shoulder.

for the homogeneous system.<sup>139-141</sup> When the supported tetrairidium catalyst was filtered from the molten salt and the  $\text{AlCl}_3\text{-NaCl}$  retested, there was no decrease in activity observed. It was proposed that the supported tetrairidium catalyst leached off the support to give the homogeneous  $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$  system. However, it was observed that prior to melting of the  $\text{AlCl}_3\text{-NaCl}$ , methyl chloride was produced. The production of methyl chloride at  $25^\circ\text{C}$  was seen to decrease with time. This decrease in production was assumed to be caused by the depletion of the  $\text{AlCl}_3\text{-NaCl}$ . The addition of anhydrous  $\text{HCl(g)}$  to the reactant gas stream rejuvenated the activity of the system for chloromethane formation. The cycling between the addition of  $\text{HCl(g)}$  and the absence of  $\text{HCl(g)}$  was done several times with no detrimental effects to the catalyst. It was reported that exposure of the activated catalyst to oxygen caused permanent deactivation of the system.

The presence of  $\text{HCl(g)}$  in the reactant stream should initiate an interaction with the remaining hydroxyl groups of the support making either  $\text{Al-Cl}$  or  $\text{Si-Cl}$  bonds and water. If this is the case, then the presence of  $\text{AlCl}_3\text{-NaCl}$  may not be necessary for the reaction to occur. Both silica gel and alumina supported clusters were tested in the presence of  $\text{HCl(g)}$  and the absence of  $\text{AlCl}_3\text{-NaCl}$ . In both cases after a 15-20 minute incubation period methyl chloride was observed at  $25^\circ\text{C}$  with the same activity and selectivity as seen previously. This induction period was suggested to be due

to the interaction of HCl with the support hydroxyl groups. These Al-Cl or Si-Cl groups are believed to behave in a similar manner as that of  $\text{AlCl}_3$ . Gas chromatography and GC/MS identified trace quantities of methane, ethylene, methyl chloride, ethyl chloride, acetaldehyde and methyl formate as reaction products. No difference was noticed



between the alumina and silica gel bound systems in regards to activity or selectivity.

The activities of the silica gel and alumina catalyst systems were shown to be dependent upon temperature. The activity of both systems increased with increasing temperature. A slight deactivation of the catalyst was observed to occur at  $100^\circ\text{C}$  over a period of time. At temperatures below  $100^\circ\text{C}$  the catalyst was observed to be stable for several days. The activity also was found to be affected by the concentration of  $\text{HCl}(\text{g})$  in the reactant gas stream. The concentration of  $\text{HCl}(\text{g})$  had to be kept at a minimum to insure catalyst stability. The comparison of metal loadings (% wt.) at various temperatures demonstrated that the catalyst activity increased with higher concentrations of iridium in the catalyst. It was noted that other factors besides the metal loading, such as support interactions, deactivation process and phosphine concentration, may influence this observed increase in activity.



Although a complete material balance wasn't obtained, a calculation using the amount of chloromethane produced relative to the other products at 100°C showed the reaction to be at least 99% selective for chloromethane. This wasn't considering a polar product that condensed along with water at the top of the reactor tube. Even though the existence of this compound was discovered using gas chromatography, the identity of the complex was not reported.

All control reactions run with or without  $\text{AlCl}_3\text{-NaCl}$  showed either little or no activity for chloromethane production as summarized in Table 3-3. A conclusion drawn from these control experiments was that the tetrairidium cluster had to be supported through a phosphine linkage for catalytic methyl chloride production to occur. It was shown that Vaskas' complex bound to a support,  $\text{Ir}(\text{PPh}_2)_2\text{IrCl}(\text{CO})$ , was slightly active for methyl chloride in the temperature range 25-100°C. This activity was far below that observed for the supported tetrairidium cluster.

It was found that other halide sources, such as  $\text{Cl}_2$ ,  $\text{HBr(g)}$  and  $\text{HCl(aq)}$  could be substituted for the  $\text{HCl(g)}$  with no decrease in initial activity or selectivity. In the case of  $\text{HCl(aq)}$  the activity was observed to decrease with time. It also was found that chloromethane production could be changed to methyl bromide by substitution of  $\text{HBr(g)}$  for  $\text{HCl(g)}$  in an active system. However, the reformation of methyl chloride by the reverse substitution of  $\text{HCl(g)}$  for  $\text{HBr(g)}$  was observed not to occur.

Table 3-3. A Summary of the Reported Activity for the Supported Iridium Carbonyl Catalyst System

Catalyst	Activity		
	25°C	100°C	145°C
$\text{Ir}_4(\text{CO})_{12} + \text{AlCl}_3\text{-NaCl}$	N.A.	-	$\text{CH}_4, \text{C}_2\text{H}_6,$ $\text{CH}_3\text{Cl}$
$\text{SG} + \text{AlCl}_3\text{-NaCl}$	N.A.	-	N.A.
$\text{SG} \sim \text{PPh}_2 + \text{AlCl}_3\text{-NaCl}$	N.A.	-	N.A.
$(\text{C}_2\text{H}_5\text{O})_3\text{Si} \sim \text{PPh}_2\text{Ir}_4(\text{CO})_{11} +$ $\text{AlCl}_3$	-	Trace $\text{CH}_3\text{Cl}$	-
$[(\text{C}_2\text{H}_5\text{O})_3\text{Si} \sim \text{PPh}_2]_2\text{Ir}_4(\text{CO})_{10}$	-	N.A.	-
$\text{Ir}_4(\text{CO})_{11}\text{PPh}_3 + \text{AlCl}_3$	-	N.A.	-
$\text{Ir}_4(\text{CO})_{12} + \text{Al} + \text{HCl}$	-	N.A.	-
$\text{Ir}_4(\text{CO})_{11}\text{PPh}_3 + \text{Al} + \text{HCl}$	-	N.A.	-
$\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 + \text{Al} + \text{HCl}$	-	N.A.	-
$\text{Al} \sim \text{PPh}_2\text{Ir}(\text{CO})\text{PPh}_3$	-	Trace $\text{CH}_3\text{Cl}$	-

N.A. = no activity; SG = silica gel; Al = alumina.

A speculative mechanism for this reaction was proposed as shown in Figure 3-1. Presumably oxidative addition of hydrogen by the supported catalyst would generate a dihydride species. Interaction of the Al-Cl or Si-Cl groups with a bound carbonyl ligand of the iridium dihydride species could induce rapid hydride migration to form a formyl complex. This is similar to the alkyl migration onto a bound carbonyl group in a  $(\text{CH}_3)_5\text{Mn}(\text{CO})_5/\text{AlBr}_3$  system as shown in Equation 3-9.<sup>153,154</sup> The reaction then could

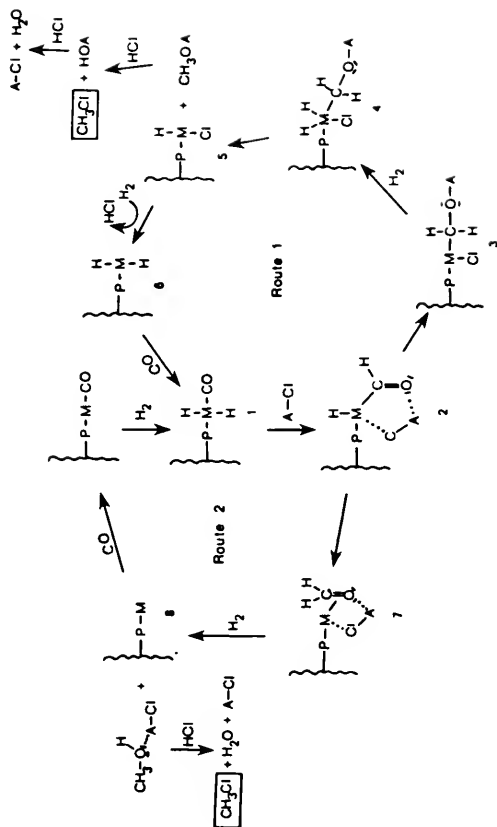
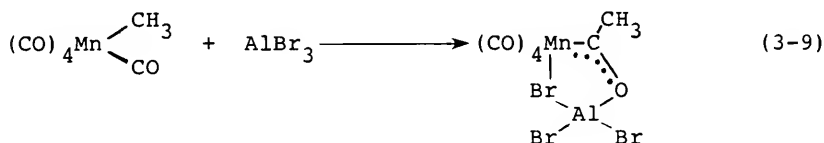
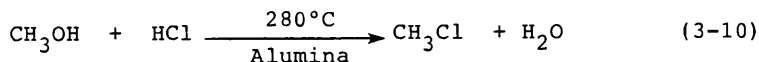


Figure 3-1. A Proposed Mechanism for the Formation of Methyl Chloride from Synthesis Gas and  $\text{HCl}$  Over a Supported Iridium Carbonyl Catalyst System (Reprinted with permission of reference 148)

proceed through the formation of a Lewis acid stabilized formaldehyde complex or a hydroxymethyl type intermediate. Finally, the formation of support  $\text{--OCH}_3$  groups or support  $\text{--(CH}_3\text{OH)}$  groups in the presence of  $\text{HCl(g)}$  would produce the observed methyl chloride.



The possibility of a methanol intermediate parallels the fact that the current industrial process for methyl chloride production involves the chlorination of methanol by  $\text{HCl}$  as shown in Equation 3-10.<sup>155</sup> Methyl chloride is a major commodity chemical with consumptions in the range of



hundreds of thousands of metric tons annually. The major uses of chloromethane include the production of methyl chlorosilanes, tetramethyl lead and butyl rubbers.<sup>155</sup> The formation of methyl chloride from synthesis gas and  $\text{HCl}$  under extremely mild conditions may be industrially useful. For this reason, a further in-depth investigation into the mechanism, as well as the optimization of this unique system is warranted.

## Experimental

### Reagents

All metal complexes were used as purchased unless otherwise stated. The  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  and all the metal carbonyl complexes were purchased from Strem Chemical Company. All solvents, except 2-methoxyethanol and 2-ethoxyethanol, were dried prior to use by distillation over  $\text{CaH}_2$ . All solvents were degassed with  $\text{N}_2$  prior to use. The alumina, acid Brockman Activity I (80-200 mesh) and the mossy zinc metal were purchased from Fisher Scientific Company. The alumina was dried at  $140^\circ\text{C}$  prior to use. This alumina was determined to have a specific area of  $180 \text{ m}^2/\text{g}$ .<sup>156</sup> The silica gel, Davison grade #62, purchased from W. R. Grace, was dried under vacuum at  $300^\circ\text{C}$  prior to use. It had a specific area of  $340 \text{ m}^2/\text{g}$ , a pore diameter of 14 mm and a pore volume of  $1.1 \text{ cm}^3/\text{g}$ . The zeolite, LZV-82, was purchased from Alfa-Thiokol. All silanes were purchased from Petrarch Chemical Company and used without purification. The carbon monoxide C. P. grade 99.5% and the hydrogen chloride technical grade 99.0% or semiconductor grade 99.995% were purchased from Matheson Gas Products. The hydrogen was obtained from Strate Welding. All carbon-13 isotopically labelled gases were purchased from Merk, Sharp and Dohme Isotopes.

### Instrumentation

All air sensitive manipulations were performed in a Vacuum Atmosphere Co. model HE-43-2 inert atmosphere box or in an Aldrich inert atmosphere glovebag. All syntheses were

performed under either a nitrogen or carbon monoxide atmosphere. GC analyses were performed on either a model 3700 FID Varian gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a 1/8 inch x 8 foot stainless steel 5% diethylene glycol adipate on chromosorb P (80/100) column or on a model 940 FID Varian gas chromatograph equipped with a 1/8 inch x 8 foot stainless steel poropak Q (100/120) column. GC mass spectrometry was performed by Dr. R. King of the Microanalytical Laboratory, University of Florida, Gainesville, Florida. Samples were run on an AEI MS 30 mass spectrometer with a KOITOS DS55 data station. The system was equipped with a PYE Unicam 104 gas chromatograph containing a 1/4 inch x 5 foot poropak Q column. Nuclear Magnetic Resonance spectra were obtained on a Varian EM360L NMR spectrometer. Infrared spectra were obtained as mulls on a Nicolet 5DXB FTIR spectrometer using KBr salt plates. All elemental analyses for carbon, phosphorous and iridium were performed by Galbraith Laboratories, Knoxville, Tennessee. All ESCA data was obtained through the courtesy of Dr. Tom Gentle, Dow Corning Corporation, Midland, Michigan. The samples were run in a Perkin-Elmer Model 551 stainless steel ultra-high vacuum chamber equipped with a dual magnesium anode x-ray source and a double pass cylindrical mirror electron analyzer. Data acquisition was controlled by a Digital PDP computer. All high pressure experiments were performed using a 50 mL Parr pressure

bottle equipped with a brass or stainless steel Swagelok pressure head.<sup>66</sup>

#### Fixed Bed Flow Reactor

A glass flow system as shown in Figure 3-2 was assembled. This was modified from the previously described system<sup>148</sup> to allow the entire gas mixture to flow through the catalyst. The individual gas flow rates were controlled by three teflon needle valves (A, B and C). The CO and H<sub>2</sub> were bubbled through mineral oil while the HCl bubbler contained sulfuric acid. The gases were allowed to flow over the catalyst which was supported on a glass frit and held in place with glass wool. The overall flow rate of the gas mixture was monitored by a bubble flowmeter. The temperature was regulated by a model 123-8 Lindberg thermostated tube furnace that surrounded the reactor tube. Gas samples for GC analyses could be obtained through two sample ports, one prior to and one after the catalyst. Gas samples were collected using a pressure-lok 2 mL syringe purchased from Precision Sampling Corporation. Gases could be trapped out through the addition of a glass spiral trap to the glass reactor system. The spiral trap allowed for maximum contact of the gas flow with the dry ice/acetone slush.

#### Preparation of Dicarbonylchloro(*p*-toluidine)iridium(I)

The IrCl(CO)<sub>2</sub>(*p*-toluidine) was prepared by a procedure similar to that reported by Klabunde.<sup>157</sup> Inside an inert atmosphere glovebag a pressure bottle system containing 1.0 g of IrCl<sub>3</sub>·3H<sub>2</sub>O, 0.30 g of lithium chloride and 50 mL of

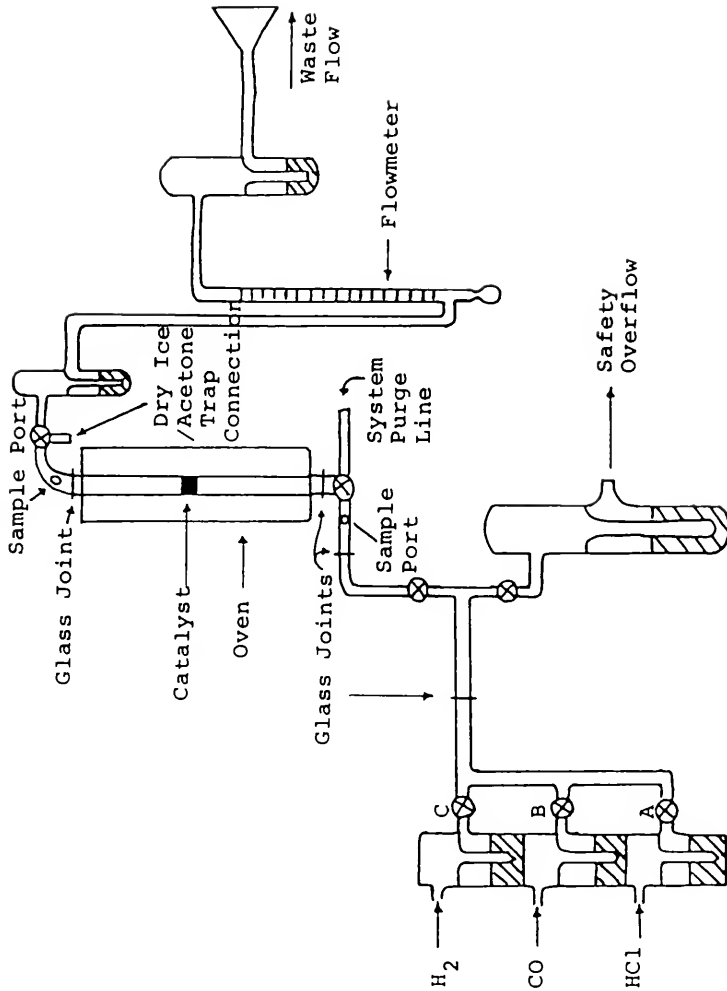


Figure 3-2. A Diagram of the Fixed Bed Flow Reactor



degassed 2-methoxyethanol was assembled. The pressure bottle was charged with 45 psig of carbon monoxide and allowed to react for several hours at 130°C. When the initial black color had changed to yellow, the pressure bottle system was cooled to room temperature. The pressure bottle was dismantled under a nitrogen atmosphere and 0.35 g of *p*-toluidine added. After several minutes of stirring, the yellow solution was poured into a beaker containing 250 mL of distilled water. A purple precipitate was formed immediately upon the mixing of the two solutions. The precipitate was collected by vacuum filtration and dried under vacuum for 24 hours. The purple solid was dissolved in a minimum amount of benzene. Then a small amount of anhydrous sodium sulfate was added to the stirred brown solution. After several hours the solution was filtered. The solvent was evaporated from the filtrate to give a purple compound which was characterized by infrared spectroscopy to be  $\text{IrCl}(\text{CO})_2(\textit{p}\text{-toluidine})$ . A typical yield was approximately 85% based on the initial  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  complex.

#### Preparation of a Phosphinated Support

The phosphinated supports were prepared by a procedure similar to that previously reported in the literature.<sup>144,145</sup> Under a nitrogen atmosphere a total of 5.0 g of a dried support, such as alumina, silica gel, or a zeolite was added to a stirred solution of 150 mL of toluene. The mixture was heated to reflux temperature prior to addition of 0.45 mL of

2-(diphenylphosphino)ethyltriethoxysilane,  $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_2\text{H}_4\text{PPh}_2$ , by a syringe method. This reaction was allowed to continue for 12 hours prior to collecting the functionalized resin by vacuum filtration. The functionalized support was dried under vacuum at room temperature for 24 hours before use. This reaction gave a phosphinated support containing  $1.25 \times 10^{-3}$  moles of accessible phosphine substituents. Supports with different phosphine concentrations were prepared in an analogous manner. In experiments where the rest of the surface was silanated with dichlorodiphenylsilane, an appropriate amount of the silane was added by syringe 6 hours after the 2-(diphenylphosphino)ethyltriethoxysilane had been added.

#### Preparation of Supported Mono- and Di-phosphine Substituted Tetrairidium Carbonyl Clusters

The phosphine substituted tetrairidium carbonyl cluster was supported by a procedure similar to that reported by Struder et al.<sup>151</sup> and Castrillo et al..<sup>152,158</sup> This procedure was adopted from one reported by Stuntz and Shapley for the formation of  $\text{Ir}_4(\text{CO})_{11}\text{PPh}_3$ .<sup>159</sup> Inside a glovebag a total of 130 mL of 2-methoxyethanol and 5 mL of water was added to a pressure bottle containing 5.0 g of a phosphinated support ( $1.25 \times 10^{-3}$  moles of phosphine) and 0.057 g of dicarbonylchloro(*p*-toluidine)iridium(I). The amount of  $\text{IrCl}(\text{CO})_2$ (*p*-toluidine) used changed according to the concentration of phosphine on the support that was used. The 15.0 g of mossy zinc metal was placed into a teflon

basket suspended in the solution above the cylindrical 1/2 inch long stirbar. The pressure bottle was charged with 45 psig of carbon monoxide and heated to 95°C. The reaction was allowed to proceed for 12 hours. The slightly yellow resin was collected by vacuum filtration, washed with approximately 75 mL of toluene and dried under vacuum for 24 hours. The catalyst prepared in other solvents, such as 2-ethoxyethanol or toluene was done in an analogous manner. The characterization of each catalyst by infrared spectroscopy is discussed in the results section.

#### Preparation of Supported Tri-phosphine Substituted Tetrairidium Carbonyl Clusters

The tri-phosphine substituted tetrairidium carbonyl cluster was supported by a procedure similar to that reported by Karel and Norton.<sup>160</sup> A total of 1.3 g of  $\text{Ir}_4(\text{CO})_{12}$  was added to a stirred toluene solution containing 5.0 g of a phosphinated support ( $1.25 \times 10^{-3}$  moles of phosphine). The reaction was allowed to proceed at reflux temperature for 24 hours. The yellow resin was collected by vacuum filtration and dried under vacuum for 24 hours. The characterization of the catalyst by infrared spectroscopy is discussed in the results section.

#### Preparation of Other Supported Phosphine Substituted Metal Carbonyl Complexes

All other metal carbonyl complexes, such as  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{IrCl}(\text{CO})_3$  and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  were supported in an analogous manner to the preparation of the supported tri-

phosphine substituted tetrairidium cluster. Appropriate amounts of the metal carbonyl complexes were added to stirred toluene solutions containing 5.0 g of a phosphinated support. The reaction was allowed to proceed at reflux temperature for 24 hours. The resins were collected by vacuum filtration and dried under vacuum for 24 hours. The characterization of each catalyst by infrared spectroscopy is discussed in the results section.

#### Preparation of Iridium Complexes Impregnated Onto a Support

The iridium complexes were impregnated onto a support through the incipient wetness impregnation of the support with a solution containing the metal complex. An appropriate amount of an iridium complex, such as  $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{Ir}(\text{CO})_3\text{Cl}$  or  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was added to a stirred cyclohexane solution containing 5.0 g of the support. The amount of metal complex added was dependent upon the concentration of iridium desired on the support. The mixture was allowed to stir at room temperature for several hours. The supported complexes were collected by vacuum filtration and dried under vacuum for 24 hours. The characterization of each catalyst by infrared spectroscopy is discussed in the results section.

#### Reaction of Catalysts with Carbon Monoxide, Hydrogen and $\text{HCl}(\text{g})$

Prior to running the catalyst experiments, the blank reactor tube was tested for any residual activity towards methyl chloride formation. Then a total of 1.0 g of a

catalyst was placed into the glass fritted reactor tube. The catalyst was held in place with glass wool. The reactor tube was placed into the fixed bed flow reactor system previously described in Figure 3-2. A typical reaction was run at 75°C with the individual  $\text{H}_2$ :CO:HCl gas flows at a ratio of 3:1:0.5 combining to give an overall flow rate of 1 mL/40 seconds. The reactant and product gases were monitored by gas chromatography. Investigation of the active catalyst by infrared spectroscopy is discussed in the results section.

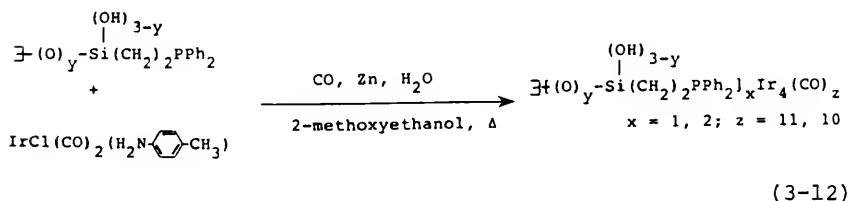
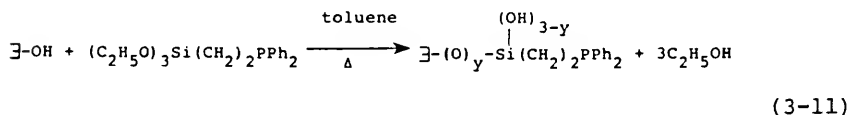
#### Reactions Involving Carbon-13 Isotopically Labelled Gases

Carbon-13 incorporation into alkyl chlorides was investigated by the reaction of carbon-13 labelled CO or  $\text{CH}_4$  gas with the catalyst in a stagnant reactor. The stagnant reactor was either a pressure bottle fit with a stainless steel Swagelok head or a closed reactor tube. In both cases, the reactor containing the catalyst was evacuated at room temperature. Then the gases were placed into the system in the appropriate ratios with the overall pressure never exceeding one atmosphere. The reaction was allowed to continue at 75°C for 24 hours. The extent of carbon-13 incorporation into the products was determined by GC mass spectrometry.

### Results and Discussion

#### Reproduction of the Previously Reported Supported Iridium Carbonyl Catalyst System

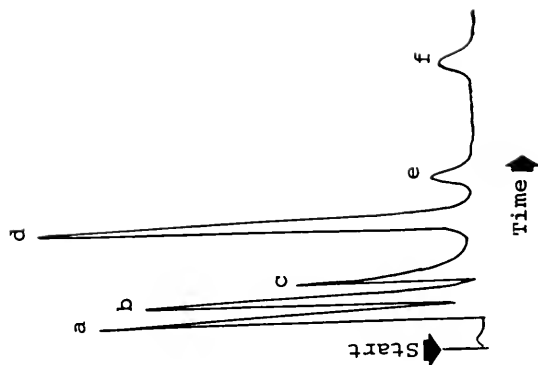
The supported tetrairidium carbonyl cluster was prepared as previously described by Miller.<sup>148</sup> First, the surface of the inorganic oxide (alumina, silica gel or zeolite) was modified by phosphine functionalization through a simple condensation reaction between 2-(diphenylphosphino)ethyltriethoxysilane and the surface hydroxyl groups as shown in Equation 3-11. Then, as shown in Equation 3-12, the supported phosphine tetrairidium carbonyl cluster was assembled through the reduction of  $\text{IrCl}(\text{CO})_2$ -(p-toluidine) by zinc metal in the presence of carbon



monoxide and a 2-methoxyethanol solvent. The catalysts were characterized by infrared spectroscopy to be a mixture of supported mono- and di-phosphine substituted tetrairidium

carbonyl clusters. A detailed discussion of the infrared data is presented later. These supported clusters were tested for catalytic activity in the presence of a 1:3:0.5 ratio of  $\text{CO}:\text{H}_2:\text{HCl}(\text{g})$  at  $75^\circ\text{C}$  in a modified fixed bed flow reactor system as described in Figure 3-2.

Similar products to those previously reported<sup>148</sup> for this reaction were identified by GC and GC/MS. A typical gas chromatogram using a poropak Q column at  $130^\circ\text{C}$  is shown in Figure 3-3. Although not shown in Figure 3-3, gas chromatography also was used to detect the presence of residual solvents, such as toluene and 2-methoxyethanol with retention times at 16 and 24 minutes, respectively. In addition, the presence of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and a trace amount of acetylene was confirmed by GC/MS. A sample of the gas mixture taken prior to the catalyst was found through the use of gas chromatography to contain methane, ethylene and ethyl chloride as the only observable impurities. The presence of these impurities was confirmed from gas specification data obtained from Matheson Gas Company for  $\text{CO}(\text{g})$  and  $\text{HCl}(\text{g})$  (technical grade).<sup>161</sup> The utilization of  $\text{HCl}(\text{g})$  (semi-conductor grade) eliminated the presence of ethylene and ethyl chloride in the pre-gas mixture. However, the presence of both ethylene or ethane and ethyl chloride was observed by gas chromatography to remain as reaction products in the post-gas mixture. It was found that if the amount of  $\text{HCl}(\text{g})$  present in the system was reduced after the



a = 0.50 minutes - methane  
 b = 0.85 minutes - ethylene  
 c = 1.20 minutes - HCl  
 d = 2.20 minutes - methyl chloride  
 e = 3.00 minutes - acetaldehyde  
 f = 5.10 minutes - ethyl chloride

Figure 3-3. A Gas Chromatogram of the Product Gases (Poropak Q Column, Attenuation = 8, Column = 130°C)



system's initial activation, the identification of methanol by gas chromatography as shown in Figure 3-4 was possible.

The initial activity for methyl chloride formation at various temperatures by the catalyst (0.31% Ir) supported on alumina was found to parallel the activity observed in the previously reported<sup>148</sup> alumina bound catalyst system,  $\text{[}\sim\text{PPh}_2\text{Ir}_4(\text{CO})_{11}$  (0.75% Ir). Actually, the 0.31% iridium catalyst that was tested showed greater initial activity than the reported 0.75% iridium catalyst as shown in Figure 3-5. This is contrary to the previously reported results which indicated that an increase in activity was associated with an increase in the metal loading of the catalyst. The consequence of this discrepancy will be discussed at a later time. It is important at this time to observe the decrease in catalyst activity associated with the second day of testing as shown in Figure 3-5. The observation of this decrease in activity was made possible through the use of a modified flow bed reactor system as described in Figure 3-2. Since this modified flow bed reactor minimized the amount of waste gas with respect to the previous flow bed reactor<sup>148</sup>, the reaction system was allowed to operate 24 hours a day. The observed decrease in activity during this time period is most likely associated with catalyst decomposition. This is supported by a first order deactivation of the catalyst system observed by Dow Chemical Company in an independent investigation of the supported catalyst.<sup>162</sup>

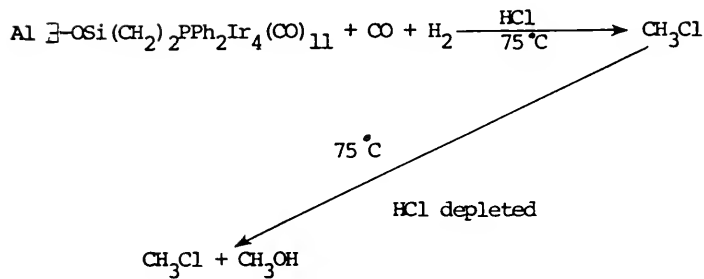
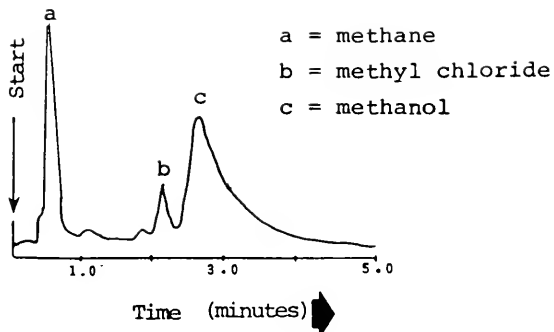
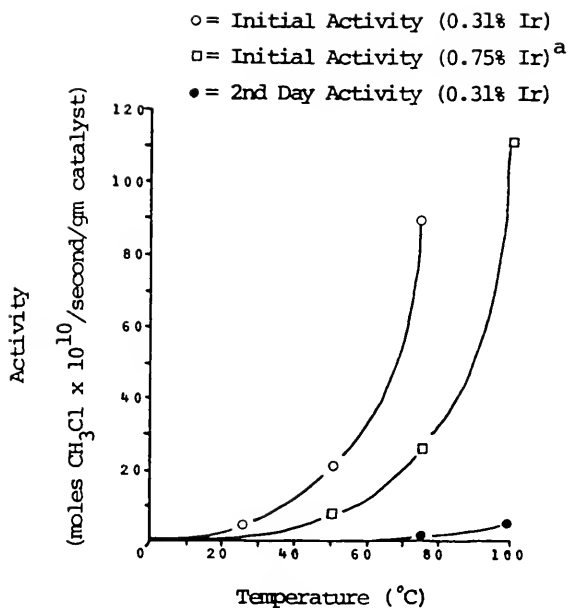


Figure 3-4. Gas Chromatography separation of Methanol and Methyl Chloride



<sup>a</sup> Data obtained from reference 148

Figure 3-5. A Graph of Catalyst Activity Versus Reaction Temperature

### Catalyst Deactivation is a Valid Observation

The catalyst deactivation observed between the initial activity (day one) and the recorded activity on the second day was monitored over an extended reaction time. It was observed that the activity of the catalyst seemed to stabilize during the third day as shown in Figure 3-6. However, this apparent stabilization was found to inherently coincide with an increase in both the  $\text{HCl(g)}$  concentration in the reactant gas and the residence time of the gas over the catalyst sample. It was found that if both of these parameters were stringently maintained at their original values, the catalyst's activity did not stabilize until after approximately ten days as shown in Figure 3-7.

The activity associated with several control reactions over an extended reaction time also is shown in Figure 3-6. The alumina control supports were prepared in the absence of any iridium precursor through a procedure analogous to the preparation of the catalyst sample. The first control reaction showed a minimal initial activity and a rapid decrease in activity with time. However, the second control reaction showed greater initial activity than the alumina supported iridium catalyst. The activity for this second control experiment seemed to level off during the third day in a similar fashion to that of the catalyst sample. The only noticeable difference in the preparation of both the alumina control supports was in the degree of solution stirring. A similar effect concerning the catalyst

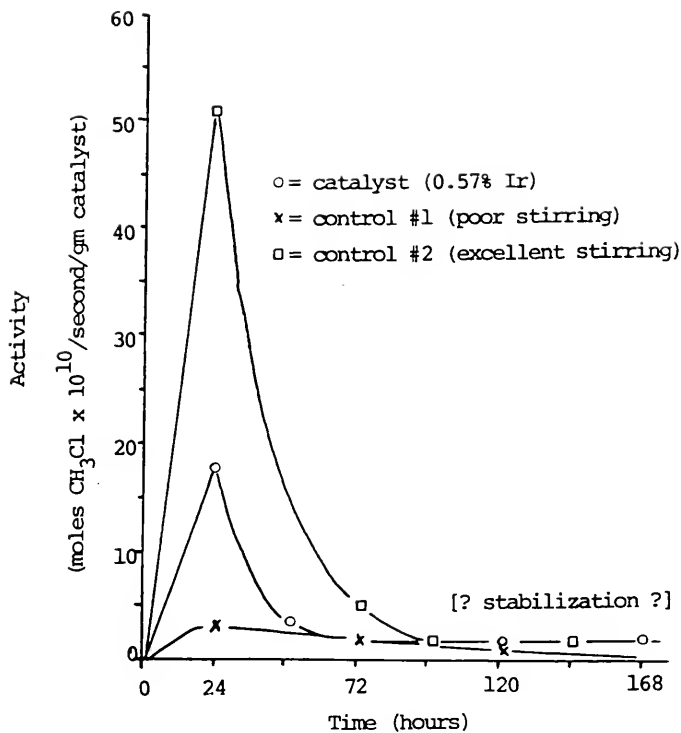


Figure 3-6. A Graph of Catalyst Activity Versus Reaction Time (Residence Time and  $\text{HCl(g)}$  Concentration was Observed to Increase with Time)

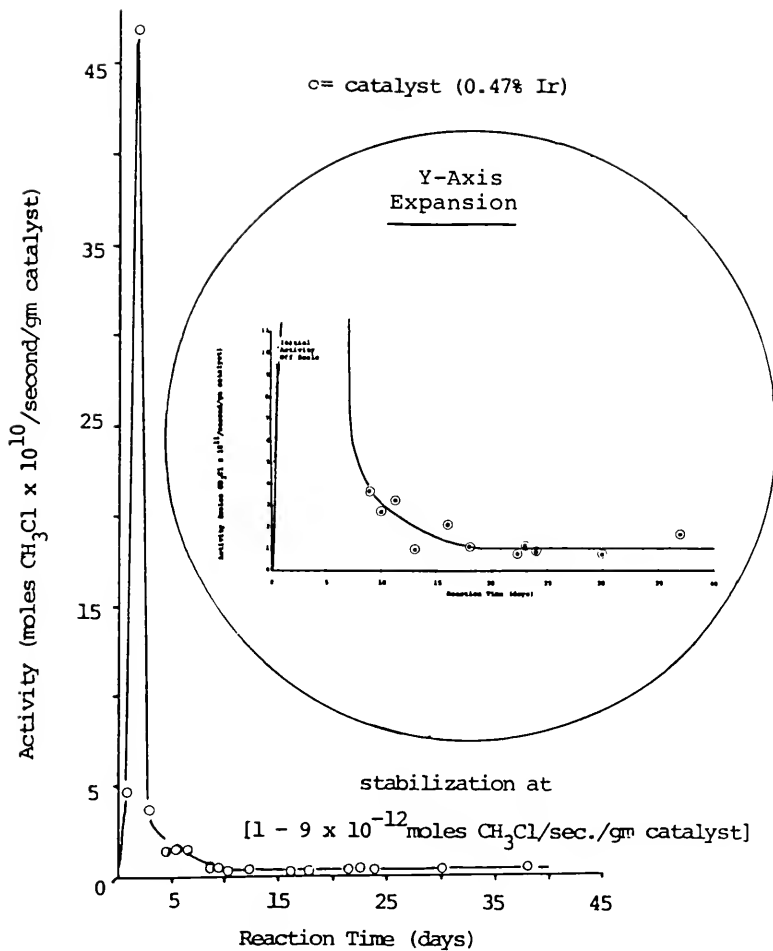


Figure 3-7. A Graph of Catalyst Activity Versus an Extended Reaction Time (Residence Time and  $\text{HCl(g)}$  Concentration Held Constant)

preparation was reported<sup>148</sup> in which poor stirring during preparation resulted in a decrease in catalyst activity. This stirring problem has been adequately disposed of by placing the desired quantity of mossy zinc in a fiberglass mesh basket suspended in the solution above the 1/2 inch cylindrical stirbar. A large number of control supports using phosphinated alumina or silica gel have been prepared under excellent stirring conditions and tested for catalytic activity towards methyl chloride formation. In each case similar activity to that observed for the supported iridium catalyst was recorded. A summary of the activity of the control supports that were run is presented in Table 3-4. When a control support was run over an extended reaction time, its activity towards the formation of methyl chloride was found to decrease to a negligible amount during the first ten days. However, the activity of the supported catalyst was observed to stabilize after ten days and persist for a period of several weeks at  $1-9 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  as shown in Figure 3-7. It should be noted that this level of activity is very close to the detection limit of the gas chromatograph. A buildup of methyl chloride over a period of twelve hours could be observed in a stagnant reactor that was formed by closing the valves on the flow reactor system. Although the occurrence of a decrease in the catalyst's activity has been verified, the cause of this decrease, as well as the cause of the activity observed in the control reactions still remains unanswered.

Table 3-4. The Initial Activity of Control Supports Prepared in 2-methoxyethanol

<u>Control Supports</u>	<u>Activity (moles CH<sub>3</sub>Cl sec<sup>-1</sup> g<sup>-1</sup>)</u>		
	<u>Day (1)</u>	<u>Day (2)</u>	<u>Day (*)</u>
Al-PPh <sub>2</sub>	2.80 x 10 <sup>-10</sup>	-	-
Al-PPh <sub>2</sub>	5.10 x 10 <sup>-9</sup>	-	2.25 x 10 <sup>-10</sup> (6)
Al-PPh <sub>2</sub>	1.57 x 10 <sup>-8</sup>	1.14 x 10 <sup>-9</sup>	1.80 x 10 <sup>-10</sup> (5)
Al/no zinc	5.18 x 10 <sup>-9</sup>	1.01 x 10 <sup>-9</sup>	1.53 x 10 <sup>-10</sup> (4)
SG	9.07 x 10 <sup>-11</sup>	-	-
SG-PPh <sub>2</sub>	2.45 x 10 <sup>-10</sup>	1.16 x 10 <sup>-10</sup>	9.45 x 10 <sup>-11</sup> (4)
Al-PPh <sub>2</sub>	3.99 x 10 <sup>-10</sup>	1.93 x 10 <sup>-10</sup>	N. A. (10)

Al = alumina; SG = silica gel; (\*) = day activity was last monitored; N. A. = no activity.

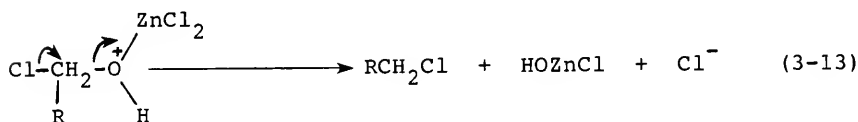
#### Investigation of the Methyl Chloride Formation Observed in the Control Reactions

Since zinc metal was used as a reducing agent in the synthesis of the supported iridium cluster, a small amount of zinc is inherently present in the support. To ascertain if this zinc metal could be responsible for the observed formation of methyl chloride, control supports were prepared in the absence of zinc, as well as the iridium precursor, through a procedure analogous to the preparation of the catalyst samples. Since these control reactions showed similar activity as compared to the supported catalyst, it



is suggested that the presence of zinc metal has no apparent effect upon the activity of the system.

Another possibility that could explain the activity observed for the control reactions is the presence of a residual amount of the 2-methoxyethanol solvent that was used in the synthesis of the supported catalyst and control supports. It is possible that an interaction between physically adsorbed or chemisorbed 2-methoxyethanol with  $\text{HCl(g)}$  could be responsible for the observed formation of methyl chloride. The cleavage of ethers and alcohols by hydrogen halides to form the corresponding alkyl halides is enhanced in the presence of a Lewis acid. This is believed to proceed through a mechanism<sup>163</sup> as shown in Equation 3-13, where the Lewis acid (i.e., Lucas reagent) coordination to the hydroxyl oxygen allows attack of the halide source upon



the electrophilic carbon through a weakening of the carbon-oxygen bond. Furthermore, the current industrial process for the production of methyl chloride has previously been shown in Equation 3-10 to involve the chlorination of methanol over an inorganic oxide support at elevated temperatures.

Several factors as shown in Table 3-5 can enhance the physical adsorption of a polar organic compound onto the surface of a hydroxylated support<sup>164</sup>. Since 2-methoxyethanol meets several of the criteria shown in Table 3-5,

Table 3-5. Factors That Enhance the Adsorption of Polar Organic Compounds onto the Surface of a Hydroxylated Support

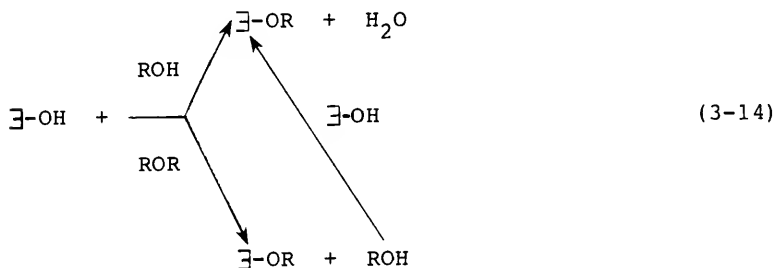
- 
- |     |   |
|-----|---|
| (1) | The presence of strong electron-donor groups (oxygen, nitrogen, etc.) |
| (2) | Increasing size and number of hydrocarbon groups in molecule.         |
| (3) | Soluble salts (NaCl, etc.) in aqueous phase.                          |
| (4) | Multiple polar groups leading to multiple surface interactions.       |
| (5) | Low temperature.  |
| (6) | A high concentration of compound to be adsorbed.                      |
- 

the adsorption of this solvent onto the surface of the support should occur quite readily. The procedure of drying the catalyst at room temperature under vacuum is not sufficient to remove this adsorbed 2-methoxyethanol.

It is well documented that the hydroxyl groups of a support, such as alumina or silica gel, will react in the presence of alcohols and ethers at temperatures exceeding 190°C to form the corresponding support bound alkoxide groups and water as shown in Equation 3-14.<sup>165,166</sup> An analogous reaction could be predicted for the chemisorption

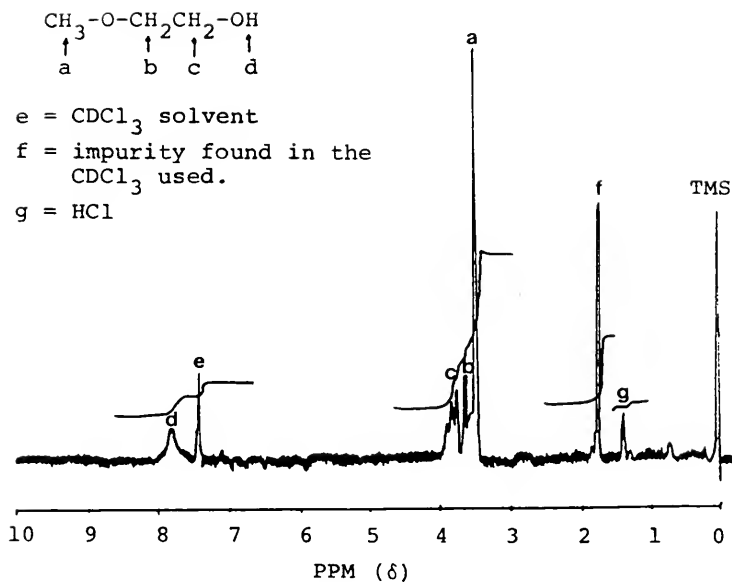
of 2-methoxyethanol onto the surface of the phosphinated support.

Recall that the presence of residual 2-methoxyethanol solvent in the catalyst reactions was observed by gas chromatography. It previously was reported that the condensation of a liquid occurred near the top of the reactor tube.<sup>148</sup> This liquid was composed of water and two unknown compounds with GC retention times of 4.16 minutes and 6.07 minutes on a DEGA column at 100°C. The larger of



the two peaks at 4.16 minutes has been identified by gas chromatography to be 2-methoxyethanol. Further identification of 2-methoxyethanol in this condensed liquid was obtained by proton NMR spectroscopy as shown in Figure 3-8. Gas chromatography results obtained by Dow Chemical Company during an in-depth investigation of the catalyst system also indicated the presence of residual 2-methoxyethanol and toluene solvents.<sup>162</sup> Since these solvent peaks were not observed by gas chromatography on the second day of catalyst activity, Dow Chemical Company

## Sample spectrum



## 2-methoxyethanol reference

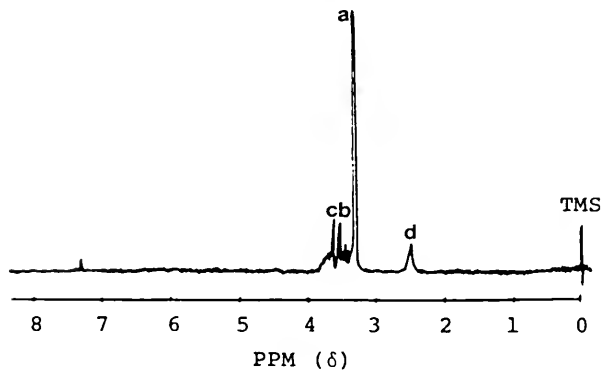


Figure 3-8. NMR Spectrum of 2-methoxyethanol that Condensed at the Top of the Reactor System

concluded that the solvent did not play a major role in the formation of methyl chloride. However, Dow Chemical Company was using higher pressures and shorter residence times than could be obtained in a glass flow reactor system. The length of time in which 2-methoxyethanol is observed is dependent upon a variety of factors, such as residence time and temperature. The presence of 2-methoxyethanol in the catalyst and control reactions employing the glass flow bed reactor has been observed by gas chromatography for periods of one to ten days. Anywhere up to a 100-fold decrease in the amount of 2-methoxyethanol present between days one and two of the catalyst's activity has been observed by gas chromatography. This decrease in activity corresponds very closely to the drop in activity for methyl chloride formation that also was observed to occur between days one and two. The cracking of physically adsorbed and chemisorbed 2-methoxyethanol present in the supported catalyst and control supports is a feasible explanation for the initial activity observed for the formation of methyl chloride.

The inability to identify by gas chromatography or GC/MS other products, such as ethylene glycol or 1,2-dichloroethane that may result from the decomposition of 2-methoxyethanol does not deter this proposal. The inability to detect these compounds may be related to the decreased sensitivity of the gas chromatograph for these products, long retention times on the GC column, the

stabilization of unidentified surface species or to the further decomposition of these compounds over the inorganic oxide supports to the observed products of methane, ethylene, methyl chloride, ethyl chloride, acetylene, methanol, carbon dioxide and water.

#### Solvent Decomposition Can Explain Other Reported and Observed Results

In order to investigate the validity of the decrease observed in the initial activity (Figure 3-5) upon an increase in metal loading, catalysts containing different iridium concentrations were prepared and tested. The results as shown in Table 3-6 indicate that an increase in the percentage of metal on the support does decrease the initial activity of the system. However, this result also can be explained by the cracking of physically adsorbed and chemisorbed 2-methoxyethanol. An increase in the metal loading of the phosphine bound catalyst must coincide with an increase in the phosphination of the support. Since the phosphination of the support proceeds through a condensation reaction of  $(C_2H_5O)_3Si(CH_2)_2PPh_2$  with the hydroxyl groups of the support, an increase in the extent of surface phosphination would result in a decrease in the number of hydroxyl groups remaining on the support. The smaller number of hydroxyl groups present in the catalyst supports containing higher metal loadings would limit the amount of 2-methoxyethanol that could be physically adsorbed or chemisorbed on the support. The overall effect would be a

Table 3-6. The Activity of Alumina Supported Tetrairidium Clusters for Various Metal Loadings

Iridium Loading (Wt. %)	Activity (moles $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$ )		
	Initial (Day 1)	Day 2	Decrease Factor Day 1 to Day 2
0.14	$2.14 \times 10^{-8}$	$5.37 \times 10^{-10}$	40
0.31	$8.90 \times 10^{-9}$	$1.11 \times 10^{-10}$	80
0.57	$2.49 \times 10^{-9}$	$2.46 \times 10^{-10}$	10
2.34	$1.04 \times 10^{-9}$	$3.10 \times 10^{-10}$	3

decrease in the activity for methyl chloride formation associated with the cracking of the smaller quantity of 2-methoxyethanol adsorbed on the support. The decrease in activity observed for the catalysts between days one and two as shown in Table 3-6 corresponds very closely to the decrease in adsorbed 2-methoxyethanol observed over the same time period by gas chromatography. Any small discrepancies in the activity calculations can be explained by the inherent errors that arise from the difficulty in maintaining the appropriate gas concentrations, a constant residence time and through interpretation of the gas chromatography calibration curves for methyl chloride.

Similarly, the differences in the initial activity of the control reactions (Figure 3-6) that arose from the difficulty in controlling the rate of stirring during the preparation of the control support can be explained through the adsorption of 2-methoxyethanol by the support. An

inadequately stirred reaction would decrease the number of hydroxyl groups that would be exposed to the 2-methoxyethanol solvent. Since these inadequately stirred reactions would result in supports containing less physically adsorbed and chemisorbed 2-methoxyethanol, they should show a smaller initial activity for the formation of methyl chloride. Since the cracking of 2-methoxyethanol governs the amount of methyl chloride initially formed, the amount of methyl chloride observed in these control reactions should be dependent upon the amount of  $\text{HCl(g)}$  present in the system and the length of the residence or contact time the gas mixture has over the control sample. As expected, an increase in the  $\text{HCl(g)}$  concentration or an increase in the residence time as shown in Figure 3-9 was found to increase the amount of methyl chloride observed in the system. It should be noted that the detection limit of the gas chromatograph for methyl chloride requires a residence time of at least 25 seconds/gram of catalyst to form an easily detectable amount of methyl chloride.

Finally, the separation of methanol observed in reactions which contained a small amount of  $\text{HCl(g)}$  as shown in Figure 3-4 could be derived from the cracking of 2-methoxyethanol to methyl chloride. Recall that the formation of water was verified by GC/MS in the catalyst reactions. The relationship between methyl chloride, water, methanol and  $\text{HCl}$  is described in Equation 3-15. A decrease in the concentration of hydrogen chloride would shift the



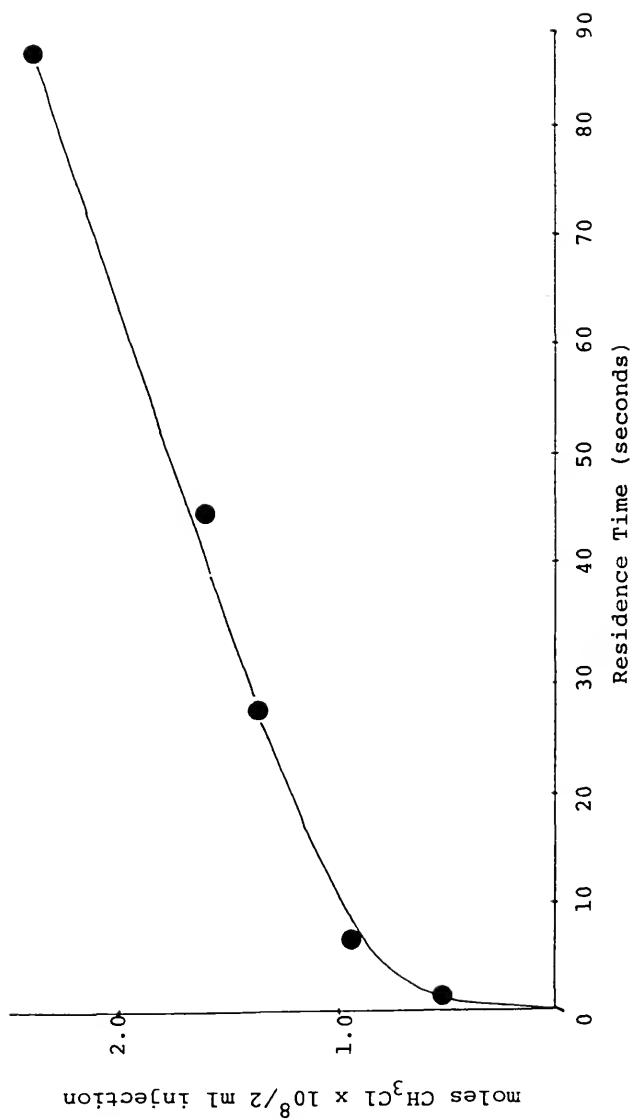
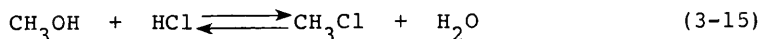


Figure 3-9. A Graph of Methyl Chloride Activity Versus Residence Time for a Reaction Involving a Control Support

equilibrium of the reaction towards the formation of methanol. The presence of this equilibrium is further supported in that the addition of water vapor to the feed



gas was observed to decrease the activity of the system towards the formation of methyl chloride.

The cracking of residual 2-methoxyethanol can explain several aspects of the catalyst system that was previously reported.<sup>148</sup> For instance, all control reactions were previously reported to be inactive towards methyl chloride formation. This can be explained by the realization that all control reactions previously run were never exposed to the 2-methoxyethanol solvent during preparation. It also was reported<sup>148</sup> that the active catalyst was oxygen sensitive. It is obvious that the cracking of the chemisorbed or physically adsorbed solvent by  $\text{HCl(g)}$  should not be affected by oxygen exposure. All catalysts that were run were found not to be air sensitive. However, the solvent can still explain this phenomena when one examines the procedure for the reported experiment.<sup>167</sup> The experiment was run at room temperature in the presence of  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$  over several days for a period of approximately eight hours per day. The system was closed and allowed to sit for ten days. A tremendous amount of methyl chloride was observed by gas chromatography to be

present at the end of this ten day period. The catalyst was exposed to air and a large decrease in activity was observed upon restarting the system in the presence of CO, H<sub>2</sub> and HCl(g). It is suggested that the presence of 2-methoxyethanol was never depleted in the initial running of the catalyst. When the system was restarted after ten days and exposed to oxygen, the decrease in the observed activity was caused by the depletion of adsorbed 2-methoxyethanol that resulted during the ten day exposure to HCl(g) in the stagnant reactor. It seems that the cracking of adsorbed 2-methoxyethanol is a feasible alternative explanation for the reported oxygen sensitivity of the catalyst.

Finally, the short incubation period that was reported<sup>148</sup> to occur prior to methyl chloride formation may be related to the cracking of 2-methoxyethanol. This incubation period was found to be related to the time required to build up an adequate concentration of methyl chloride in the system which could be observed by gas chromatography. This is supported by the observation that the length of time associated with this incubation period could be altered by changing either the HCl(g) concentration in the system or the contact time between the gases and the catalyst. Thus, the cracking of physically adsorbed and chemisorbed 2-methoxyethanol can adequately explain the observed initial activity, as well as the reported oxygen

sensitivity and incubation period of the catalyst and control reactions.

#### The Reduction of Carbon Monoxide Still Occurs

Recall that the stabilization of the activity at  $1-9 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  as shown in Figure 3-7 occurred after approximately the tenth day of running the catalyst system. It is possible that this stabilization in activity results from the conversion of synthesis gas and  $\text{HCl(g)}$  over the supported iridium catalyst to methyl chloride. This is supported by the thermodynamic feasibility of the conversion of synthesis gas and  $\text{HCl(g)}$  to methyl chloride as shown in Table 3-7.

Table 3-7. Thermodynamic Data for Reactions Involving Synthesis Gas Reduction

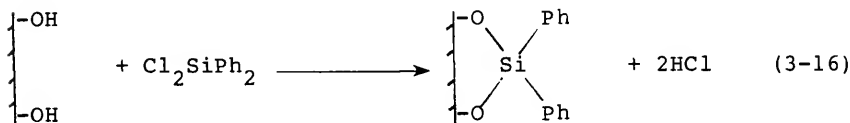
Reaction	$\Delta H_{298}^{\circ}$ (kcal mole <sup>-1</sup> )
$\text{CO} + 2\text{H}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}$	-28.9
$\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$	-21.7
$\text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$	-49.3
$2\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_4 + \text{CO}_2$	-59.1

In order to investigate if the iridium bound catalyst was reducing carbon monoxide, experiments were conducted with the goal of eliminating the activity associated with the 2-methoxyethanol solvent. First, elimination of the solvent was attempted by washing the supported catalyst and

the control supports with 2-ethoxyethanol, ethanol or methylene chloride. In each case, a 10 to 100-fold decrease in the initial activity was observed. This diminished activity is associated with the partial removal of the adsorbed 2-methoxyethanol solvent. In the case of the methylene chloride wash, the separation of adsorbed metal carbonyl complexes from the supported iridium carbonyl clusters was observed by infrared spectroscopy. The complete removal of the adsorbed 2-methoxyethanol was attempted by washing the catalyst with water and by heating the catalyst under vacuum. It was shown by infrared spectroscopy that washing the catalyst with water hydrolyzed the bound cluster off of the support through attack upon the silane linkage. Subjecting the catalyst to elevated temperatures under vacuum was found by infrared spectroscopy to decompose the tetrairidium carbonyl cluster.

An experiment designed to block the reaction between 2-methoxyethanol and the surface hydroxyl groups was performed. The phosphinated support prior to contact with 2-methoxyethanol was reacted with dichlorodiphenylsilane in an attempt to silanate the rest of the support's surface. This silanation process proceeds through the reaction of the support hydroxyl groups with the silicon-chloride linkages of the silane as shown in Equation 3-16. The decrease in methyl chloride activity observed for this silanated support can account only for the partial elimination of the adsorbed

2-methoxyethanol. It is possible that complete silanation of the support's surface was not obtained because of the steric effect associated with the phenyl groups of the



silane. Data concerning the duration of the activity associated with this silanated support was not obtained.

In order to substantiate the cluster's activity, attempts were made to synthesize the supported cluster in the absence of 2-methoxyethanol. The infrared data obtained for these supported iridium complexes will be discussed at a later time. Testing the supported iridium complex (0.99% Ir) made in 2-ethoxyethanol in either a flow reactor or a stagnant reactor system showed an activity of  $4.34 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$ . It was found that using supports containing different iridium loadings, such as 1.92% and 0.99%, showed little affect upon the system's activity. Gas chromatography also was used to identify large amounts of methane and either ethane or ethylene and trace quantities of acetaldehyde and ethyl chloride as reaction products. The separation of ethane from ethylene by gas chromatography was not obtained. It was noticed that the concentration of acetaldehyde was found to increase with higher reaction temperatures.

Testing the supported iridium complex (1.18% Ir) prepared in toluene showed similar activity to that observed for the 2-ethoxyethanol prepared catalyst. An initial surge in activity was observed during the first day of activation as shown in Figure 3-10. The activity was found to level off after the first day at approximately  $7.80 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$ . A similar surge in activity was observed for the supported cluster exposed to a reactant gas stream consisting of only  $\text{H}_2$  and  $\text{HCl(g)}$ . This suggests that this surge in activity can be associated with the conversion of coordinated carbonyl groups during the decomposition of the supported cluster. This is further substantiated by the identification of methyl chloride, ethyl chloride, water, carbon dioxide and a trace amount of acetylene in experiments using isotopically labelled carbon-13 carbon monoxide. The mass intensity report for acetylene is shown in Figure 3-11. A total of 1.4% carbon-13 incorporation above natural abundance into methyl chloride, as well as between 32-45% incorporation of carbon-13 into carbon dioxide was observed by GC/MS. The incorporation of any carbon-13 into ethyl chloride could not be detected by GC/MS. The small amount of incorporation of carbon-13 into methyl chloride is not surprising since the original supported iridium clusters contain entirely carbon-12 carbonyl ligands. The 55-68% carbon-12 carbon dioxide that was observed may arise from either the decomposition of the cluster or a water-gas shift mechanism. This water-gas

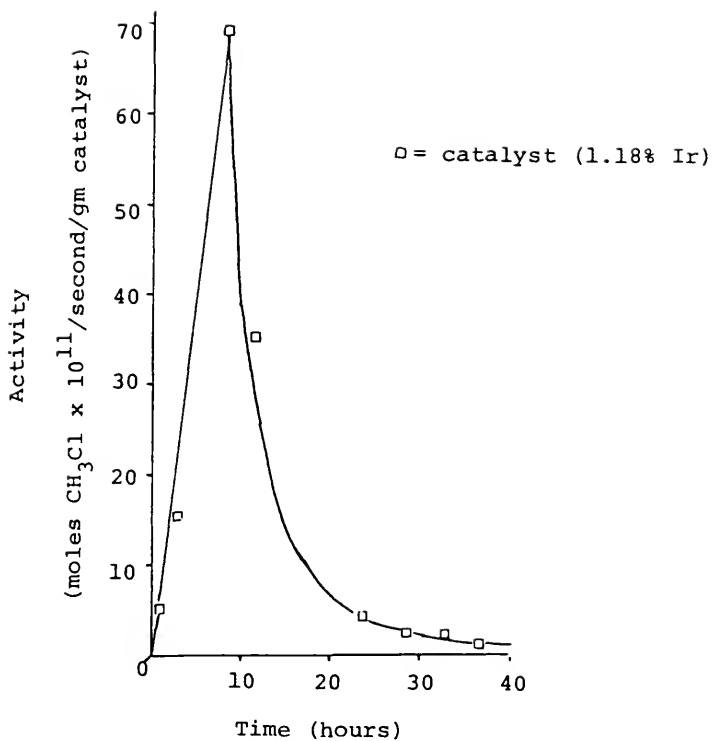


Figure 3-10. A Graph of Initial Methyl Chloride Activity Versus Time for a Catalyst Prepared in Toluene



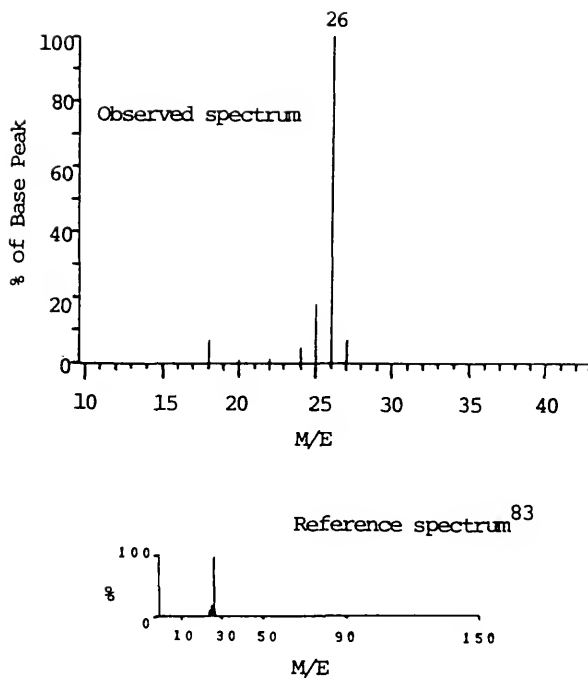


Figure 3-11. Mass Intensity Report for Acetylene

shift mechanism would involve the substitution of carbon-13 carbon monoxide for carbon-12 carbonyl groups in the cluster followed by the subsequent activation of the resulting carbon-12 carbon monoxide over the hydroxylated inorganic oxide support. The absence of carbon-13 incorporation into ethyl chloride suggests that the ethyl chloride is formed from  $\text{HCl(g)}$  attack upon surface ethoxide groups. The presence of surface ethoxide groups arises from the reaction of the surface hydroxyl groups with the ethanol that is inherently produced during the phosphination of the support as shown in Equation 3-11.

Another method of catalyst preparation involved the substitution of a carbonyl ligand in  $\text{Ir}_4(\text{CO})_{12}$  with a phosphine group of the functionalized support. It has been reported that this reaction performed in toluene produces entirely the triphosphine substituted tetrairidium carbonyl cluster.<sup>160</sup> This supported cluster (1.48% Ir) was observed by gas chromatography to produce methyl chloride, acetaldehyde and ethyl chloride. The cluster's activity for the formation of methyl chloride was found to be  $6.35 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  at  $75^\circ\text{C}$ . This activity increased to  $2.11 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  upon raising the temperature to  $200^\circ\text{C}$ . The activity observed for this supported cluster and the other supported clusters prepared in the absence of 2-methoxyethanol supports the formation of the methyl chloride through the reduction of carbon monoxide. It is proposed that this activity of  $1-9 \times$

$10^{-12}$  moles  $\text{CH}_3\text{Cl}$   $\text{sec}^{-1} \text{ g}^{-1}$  associated with the supported clusters is due to the conversion of bound carbonyl groups and the reduction of carbon monoxide. Since this activity is considerably less than previously thought, the total amount of methyl chloride produced in a 40-day period is below one catalyst ( $\text{E-P}_x\text{Ir}_4(\text{CO})_y$ ) turnover. Therefore, a discussion concerning the catalytic ability of the system will not be undertaken.

#### Minor Impurity Routes to Methyl Chloride

Several control reactions employing inorganic oxide supports either prior to or after phosphination in solvents other than 2-methoxyethanol were run. A large amount of methane, ethylene or ethane, ethanol, ethyl chloride and acetaldehyde was observed by gas chromatography for a control support which had been prepared in 2-ethoxyethanol. A trace amount of methyl chloride also was observed by gas chromatography over a short period of time at  $125^\circ\text{C}$ . In general, it seems that whenever ethanol or ethyl chloride is present, small quantities of acetaldehyde, ethylene or ethane and methyl chloride are observed. It also was noticed that the presence of  $\text{HCl(g)}$  is required for the formation of these products. The formation of these products was observed to be more dramatic for inorganic oxides of increasing acidity,<sup>123</sup>  $\text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{Zeolite}$ . The quantity of these products was observed to depend upon the amount of ethanol or ethyl chloride initially present. A similar observation has been reported for control

reactions involving  $\text{HCl(g)}$  and  $\text{AlCl}_3$  at elevated temperatures.<sup>168</sup> This suggests that the ethylene, acetaldehyde, as well as the trace quantity of methyl chloride arises from the decomposition of either ethanol or ethyl chloride. The ethanol and ethyl chloride most likely arises from the surface ethoxide groups formed during support phosphination, as well as from adsorbed 2-ethoxyethanol solvent.

A reaction scheme consistent with these observed results can be proposed from the available literature. Several reports indicate that ethanol can be converted at elevated temperatures over inorganic oxides to ethylene,<sup>169-171</sup> ethane<sup>169</sup> and acetaldehyde<sup>171</sup> or over supported metal catalysts to ethylene<sup>172</sup> and acetaldehyde.<sup>172,173</sup> This reaction scheme is complicated in that these decomposition products of ethanol can interconvert under the reaction conditions employed. For instance, ethylene over aluminum trichloride in the presence of  $\text{HCl(g)}$  has been reported to form ethyl chloride.<sup>174</sup> It also has been found that acetaldehyde is a by product in the direct hydration of ethylene to ethanol.<sup>174</sup> Finally, hydrocarbon cracking reactions were suggested to be occurring in the homogeneous  $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$  system.<sup>140</sup>

Similar reasoning gives a possible explanation for the observed formation of methyl chloride. It has been reported that ethylene decomposes to acetylene over various metal surfaces.<sup>175-177</sup> Recall that a trace quantity of acetylene





was identified by GC/MS in the reactions involving the supported cluster. Acetylene chemisorbed onto a support has been reported to decompose to carbon atoms between 25-125°C.<sup>177</sup> A similar carbon bond rupture has been postulated for the chemisorption of acetylene onto a hydrogenated iridium surface.<sup>178</sup> The formation of other one carbon species, such as formaldehyde and carbon monoxide has been reported for the oxidation of acetylene over palladium black.<sup>179</sup> It is possible that either formaldehyde or other reduced carbon species on the inorganic oxide support could form methyl chloride in the presence of hydrogen and HCl(g). This is supported by the observation that formaldehyde and HCl(g), over a zeolite, produces a mixture of methyl chloride and methylene chloride.<sup>180</sup>

Several control reactions using a phosphinated support prepared in toluene showed the formation of a trace quantity of methyl and ethyl chloride. The lifetime and the amount of activity of these control resins was observed to be reduced as compared to the control resins prepared in 2-ethoxyethanol. The formation of the ethyl chloride is assumed to arise from the ethoxide groups on the support which were formed during the phosphination procedure. The formation of the trace quantity of methyl chloride is proposed to arise from the decomposition of toluene adsorbed onto the support. Recall that the presence of residual toluene in the supported cluster reactions was confirmed by GC/MS. It previously has been reported that toluene is

converted in 50% yield to benzene and methane at 400°C over a supported iridium metal catalyst.<sup>181</sup> A similar conversion of toluene to benzene and methane has been reported for a supported platinum metal catalyst.<sup>182</sup> In this case, an increase in activity was observed by pretreating the support with HCl(g). Furthermore, it is thermodynamically possible that toluene could decompose totally to methane or to carbon atoms as shown in Table 3-8.<sup>181</sup> It is possible that an interaction of these reduced carbon species with hydrogen and HCl(g) could produce the trace quantity of methyl chloride observed over a short period of time in these control reactions.

The proposed explanation for the low level formation of the products observed in the control reactions prepared in

Table 3-8. Thermodynamic Data Concerning the Decomposition of Toluene

Reaction		$\Delta H_{298}^{\circ}$ (kJ Mole <sup>-1</sup> )
 -CH <sub>3</sub> + H <sub>2</sub>	$\longrightarrow$  + CH <sub>4</sub>	-42.0
 -CH <sub>3</sub> + 10H <sub>2</sub>	$\longrightarrow$ 7CH <sub>4</sub>	-574.3
 -CH <sub>3</sub>	$\longrightarrow$ 7C + 4H <sub>2</sub>	-49.8

2-ethoxyethanol or toluene is supported by the presence of several impurities inherent to the reactant gases. It has been reported that a 600 ppm impurity of oxygen is present in the carbon monoxide gas that was used.<sup>183</sup> A low level

impurity of methane in this CO feed gas also was identified by gas chromatography. The technical grade HCl(g) has been reported to contain a 0.4 weight percent hydrocarbon impurity which consists of a mixture of ethylene, 1,1-dichloroethane and ethyl chloride.<sup>183</sup> On the other hand, the semiconductor grade HCl(g) was reported to contain only a 10 ppm methane impurity.<sup>183</sup> The formation of ethylene, acetaldehyde, ethyl chloride and methyl chloride still was observed for the reaction of the phosphinated support with carbon monoxide, hydrogen and the semiconductor grade HCl(g). In this case, ethylene was found not to be present in the reactant gas mixture. Schwartz and Kitajima have reported the conversion of methane and HCl(g) to methyl chloride over supported rhodium complexes.<sup>184</sup> The supported iridium clusters were tested in the presence of  $^{13}\text{CH}_4$ , HCl,  $\text{H}_2$  and CO. The incorporation of carbon-13 into methyl chloride could not be substantiated by the results obtained by GC/MS.

One last possible carbon source for methyl chloride formation that must be considered is the ethyl chain and phenyl groups of the phosphinated silane linkage. The  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2\text{PPh}_2$  support linkage has carbon-carbon stretches in the phenyl groups which exhibit infrared absorptions at 1587(s) and 1572(w)  $\text{cm}^{-1}$  as shown in Figure 3-12. These infrared absorptions have been observed in the infrared spectra obtained for supports that have been phosphinated with the silane linkage and subsequently

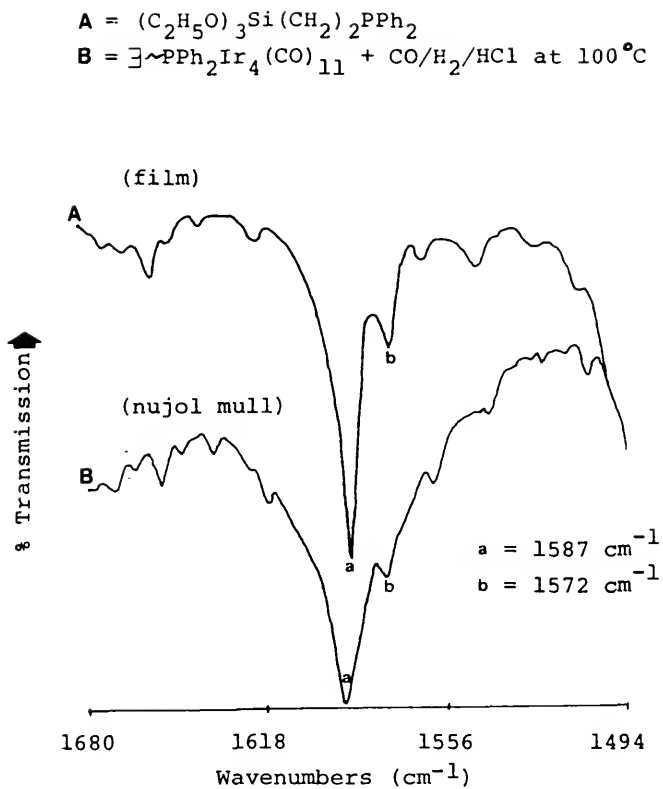


Figure 3-12. Infrared Spectrum of the C=C Vibrations in the Phenyl Groups of the Silane Linkage



functionalized with the iridium cluster. However, these infrared absorptions observed for the supported silane linkage are much broader and not as intense as those observed for the homogeneous complex,  $(C_2H_5O)_3Si(CH_2)_2PPh_2$ . This effect is associated with the occurrence of a broad absorption in this region due to the support, as well as water vapor. Upon activation of the supported cluster with CO,  $H_2$ , and  $HCl(g)$ , the infrared absorptions assigned to the phenyl groups of the phosphine linkage were observed to increase in intensity. The infrared spectrum in this region of an activated supported iridium carbonyl cluster is shown in Figure 3-12. The presence of these absorptions at 1587 and  $1572\text{ cm}^{-1}$  in the activated sample of the supported iridium carbonyl cluster suggests that the phosphine linkage is not attacked by the  $HCl(g)$  feed gas. Therefore, it is doubtful that decomposition of the phosphine linkage is responsible for the formation of any of the observed reaction products.

The preceding observations indicate that there exists a variety of inherent minor impurity routes through which methyl chloride may be formed. These minor routes can account for some of the initial activity observed in the supported cluster reactions for the formation of methyl chloride and the other observed products. It is proposed that after approximately the first several days the activity of  $1.9 \times 10^{-12}$  moles  $CH_3Cl\text{ sec}^{-1}\text{ g}^{-1}$  observed for the supported cluster prepared in the absence of

2-methoxyethanol results predominantly from the conversion of bound carbonyl groups and the reduction of carbon monoxide.

Structural Determination of the Supported Iridium Clusters by Infrared Spectroscopy

The supported iridium carbonyl cluster prepared through the reduction of  $\text{IrCl}(\text{CO})_2(\rho\text{-toluidine})$  in 2-methoxyethanol was identified by infrared spectroscopy to be a mixture of the mono- and di-phosphine substituted tetrairidium carbonyl clusters. All infrared data obtained for the synthesis of these iridium clusters in various solvents is summarized in Table 3-9. The infrared spectra for the supported iridium clusters prepared through the reduction of  $\text{IrCl}(\text{CO})_2(\rho\text{-toluidine})$  in 2-ethoxyethanol or toluene did not identically match the spectra obtained for the supported clusters prepared in 2-methoxyethanol. A mixture of mono-di- and tri-phosphine substituted tetrairidium carbonyl clusters were identified by infrared spectroscopy for the supported clusters prepared in 2-ethoxyethanol. The tri-phosphine substituted iridium carbonyl cluster was the predominant species identified in the reactions involving toluene as the solvent. The remaining infrared absorption at  $1960\text{ cm}^{-1}$  in both cases can be assigned to a supported mononuclear or dinuclear iridium species, such as  $\text{E-PPH}_2\text{IrCl}(\text{CO})_2$  or  $\text{E-}[\text{PPH}_2\text{Ir}(\text{CO})_3]_2$ . The formation of a mononuclear species most likely could arise through the substitution of the para-toluidine ligand in  $\text{IrCl}(\text{CO})_2-$

(*p*-toluidine) with the supported phosphine,  $\Xi\text{-OSi(CH}_2)_2\text{PPh}_2$ . It also has been reported that the reduction of  $\text{IrCl(CO)}_2\text{-(}i\text{-toluidine)}$  in the presence of excess triphenylphosphine leads to the formation of  $[\text{Ir(CO)}_3\text{PPh}_3]_2$ .<sup>158</sup> An analogous reaction could be suggested to form a supported dinuclear species, such as  $\Xi\text{-[PPh}_2\text{Ir(CO)}_3]_2$ .

The formation of this supported dinuclear species, may be a result of trapping an intermediate complex that normally would lead to the formation of a tetranuclear iridium cluster. It has been proposed that the conversion of  $\text{IrCl(CO)}_2(i\text{-toluidine})$  into phosphine substituted tetrairidium carbonyl clusters proceeds through the formation of iridium dinuclear complexes.<sup>159</sup> This proposal is supported by the reported conversion of  $[\text{Ir(CO)}_3\text{PPh}_3]_2$  into  $\text{Ir}_4(\text{CO})_9(\text{PPh}_3)_3$ ,<sup>185</sup> as well as the formation of  $\text{Ir}_4(\text{CO})_{12}$  from  $\text{Ir}_2(\text{CO})_8$ .<sup>186</sup> Similarly, the formation of a mononuclear species, such as  $\Xi\text{-PPh}_2\text{Ir(CO)}_2\text{Cl}$  could be related to the trapping of a reaction intermediate. This is suggested by the reported formation of  $\text{Ir}_4(\text{CO})_{12}$  from the anion  $[\text{Ir(CO)}_2\text{Cl}_2]^-$ .<sup>187</sup>

The predominant species identified by infrared spectroscopy for the supported cluster prepared in toluene through phosphine substitution of the carbonyl ligands in  $\text{Ir}_4(\text{CO})_{12}$  was the tri-phosphine substituted tetrairidium carbonyl cluster. The observed infrared spectrum for this supported cluster is shown in Figure 3-13. Attempts to isolate either mono- or di-phosphine substituted

Table 3-9. A Summary of the Infrared Data Obtained for the Supported Iridium Clusters

Complex	Infrared Data (cm <sup>-1</sup> )	Assignments	Environment	Reference
$\text{Ir-P}_x\text{Ir}_4(\text{CO})_y$ (2-methoxyethanol) <sup>a</sup>	2083(w), 2070(w), 2051(s), 2030(s), 2020(s), 2000(s), 1845(w), 1825(m), 1795(w)	Mixture of $\text{Ir-P}_3\text{Ir}_4(\text{CO})_{11}$ $\text{Ir-P}_2\text{Ir}_4(\text{CO})_{10}$	nujol	b (Fig. 3-14)
$\text{Ir-P}_x\text{Ir}_4(\text{CO})_y$ (2-ethoxyethanol) <sup>a</sup>	2051(s), 2037(s), 2021(s), 2000(s), 1996(s), 1960(m), 1821(m)	Mixture of $\text{Ir-P}_3\text{Ir}_4(\text{CO})_{11}$ $\text{Ir-P}_2\text{Ir}_4(\text{CO})_{10}$ $\text{Ir-P}_3\text{Ir}_4(\text{CO})_9$ $\text{Ir-P}_2\text{IrCl}(\text{CO})$	nujol	b (I)
$\text{Ir-P}_x\text{Ir}_4(\text{CO})_y$ (Toluene) <sup>a</sup>	2042(s), 1995(s), 1960(s)	Mixture of $\text{Ir-P}_3\text{Ir}_4(\text{CO})_9$ $\text{Ir-P}_2\text{IrCl}(\text{CO})$ $\text{Ir-P}(\text{Ir}(\text{CO})_3)_2$	nujol	b(III)
$\text{Ir-P}_x\text{Ir}_4(\text{CO})_y$ (Toluene) <sup>c</sup>	2045(s), 1995(vs), 1791(m), 1774(w),	$\text{Ir-P}_3\text{Ir}_4(\text{CO})_9$	nujol	b (Fig. 3-13)
$\text{Ir-P}_x\text{Ir}_4(\text{CO})_y$ -SiPh <sub>3</sub> (Toluene) <sup>c</sup>	2083(w), 2039(vs), 2025(s), 1845(w), 1827(w)	Mixture of $\text{Ir-P}_3\text{Ir}_4(\text{CO})_{11}$ $\text{Ir-P}_2\text{Ir}_4(\text{CO})_{10}$	nujol	b (Fig. 3-14)
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	1952(vs)		nujol	b (III)
$[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$	1960(vs)		-	188
$\text{Ir-P}_3\text{Ir}_4(\text{CO})_{11}$	2090(m), 2061(m), 2023(m), 1845(m), 1825(m)		wafer	151, 189
$\text{Ir-P}_2\text{Ir}_4(\text{CO})_{10}$	2074(s), 2050(vs), 2017(m)		wafer	151
$\text{Ir-P}_3\text{Ir}_4(\text{CO})_9$	2087(w), 2045(s), 1998(vs), 1790(s)		membrane	158, 190

a: cluster formed by reduction of  $\text{IrCl}(\text{CO})(p\text{-toluidine})$ ; b = this work; c = cluster formed by substitution of carbonyl ligand in  $\text{Ir}_4(\text{CO})_{12}$ ; (I-III) = location of infrared spectrum in appendix B.

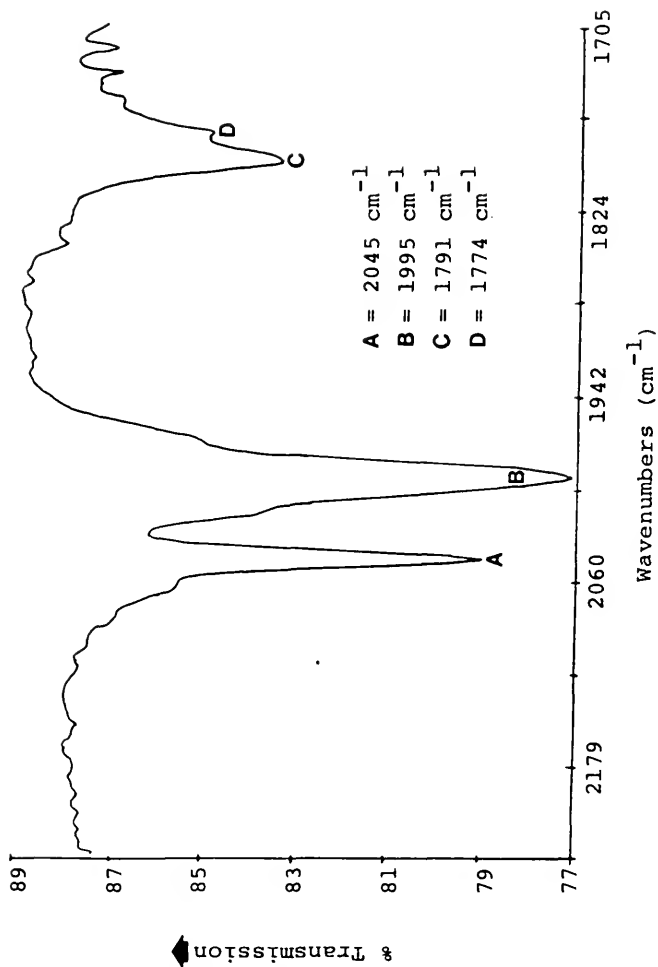
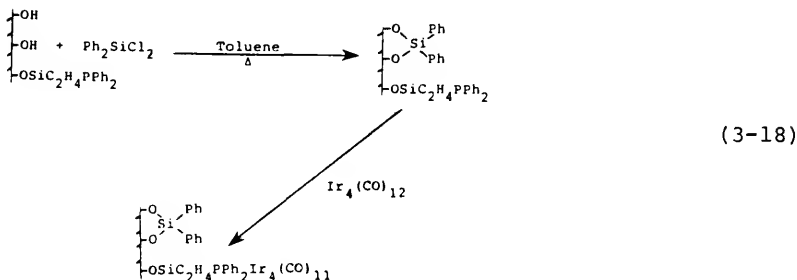


Figure 3-13. Infrared Spectrum of  $[-(\text{PPh}_2)_3\text{Ir}_4(\text{CO})_9]$  Obtained From the Reaction of  $[-\text{PPh}_2]$  with  $\text{Ir}_4(\text{CO})_{12}$

tetrairidium carbonyl clusters by this procedure have been unsuccessful. The isolation of predominantly the tri-phosphine substituted iridium carbonyl cluster is a result of the rate acceleration for CO dissociation observed for progressive phosphine substitution of carbonyl ligands in  $\text{Ir}_4(\text{CO})_{12}$ .<sup>190-192</sup> Interpretation of the infrared data shown in Table 3-9 suggests that the formation of the mono-phosphine tetrairidium carbonyl cluster has been obtained only when the cluster was prepared in 2-methoxyethanol. It has been reported that the mono-phosphine substituted tetrairidium cluster shows greater activity than the di- or tri-phosphine substituted clusters towards olefin hydrogenation.<sup>193</sup> Analogously, it could be argued that the mono-phosphine substituted tetrairidium carbonyl cluster is more active than the di- or tri-phosphine substituted clusters for the conversion of synthesis gas and  $\text{HCl(g)}$  into methyl chloride.

To ascertain the validity of this argument, further attempts to prepare the supported mono-phosphine iridium carbonyl cluster in a solvent other than 2-methoxyethanol were done. It was found that a mixture of mono- and di-phosphine tetrairidium carbonyl clusters could be obtained in toluene using a phosphinated support in which the remaining hydroxyl groups of the surface had been silanated with  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  as shown in Equation 3-18. It seems that the size of the surface phenyl groups

sterically hinders the phosphine substitution of more than two carbonyl groups in  $\text{Ir}_4(\text{CO})_{12}$ . The comparison of the infrared spectrum for the supported clusters prepared in



this manner with the spectrum of the supported clusters prepared in 2-methoxyethanol is shown in Figure 3-14. Although a high percentage of the di-phosphine substituted tetrairidium carbonyl cluster is present in this sample, the existence of the mono-phosphine substituted tetrairidium carbonyl cluster is suggested by the presence of the bridging carbonyl infrared adsorption at  $1845\text{ cm}^{-1}$ . It is predicted that utilizing a smaller ratio of support phosphination: support silanation that the mono-phosphine tetrairidium carbonyl cluster may be formed exclusively. This was not investigated since the resulting iridium carbonyl cluster concentration would be below the available infrared detection limits. Testing this mixture of supported mono- and di-phosphine iridium carbonyl clusters for synthesis gas conversion resulted in an activity of  $6.21 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  at  $75^\circ\text{C}$ . This activity is

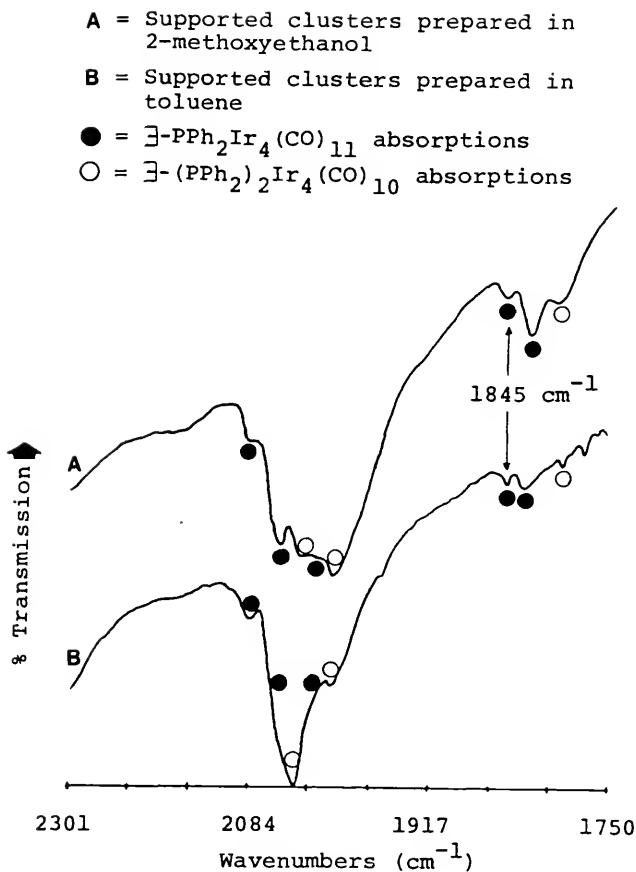


Figure 3-14. A Comparison of the Infrared Spectra of the Mono- and Di-phosphine Substituted Tetrairidium Carbonyl Clusters Prepared in 2-methoxyethanol and toluene



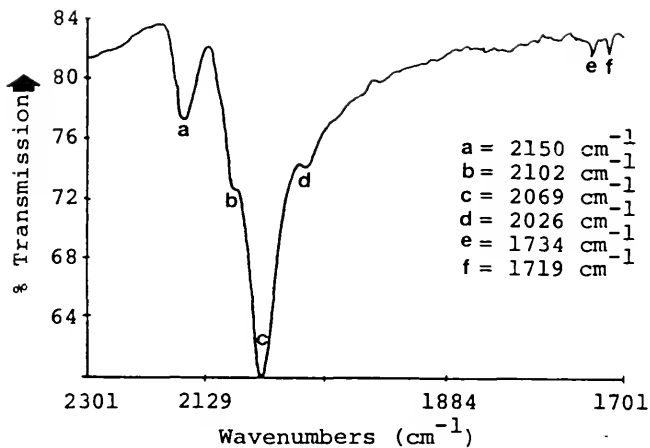
very similar to the activity previously observed for the supported clusters,  $\text{Zr-PPh}_2\text{Ir}_4(\text{CO})_{10}$  and  $\text{Zr-PPh}_3\text{Ir}_4(\text{CO})_9$ , prepared in either 2-ethoxyethanol or toluene. Therefore, it is proposed that the mono-, di- and tri-phosphine substituted tetrairidium carbonyl clusters under the same reaction conditions either show similar activity or act as precursors to iridium species that show similar activity for the formation of methyl chloride. All data discussed in the following sections concern supported complexes or control supports that have been prepared in the absence of 2-methoxyethanol.

#### Examination of the Decomposition of the Supported Clusters by Infrared Spectroscopy

Infrared spectroscopy was used to investigate the possibility that the supported iridium clusters may have been converted to other iridium species upon exposure to synthesis gas and  $\text{HCl(g)}$  at  $75^\circ\text{C}$ . All of the activated supported clusters, either the mono-, di- or tri-phosphine substituted iridium carbonyl clusters, showed a predominant absorption in the infrared spectrum at either 2069 or  $2040\text{ cm}^{-1}$  after exposure to the reactant gas mixture. The positioning of the predominant absorption in the infrared spectrum at 2069 or  $2040\text{ cm}^{-1}$  was observed to be dependent upon the weight percentage of iridium present and not upon the nature of the initial cluster. The typical infrared spectra that were obtained are shown in Figure 3-15. If the iridium weight percentage was below approximately 1.00% (low

(A)

High Load System - (2.34% Ir)



(B)

Low Load System - (0.37% Ir)

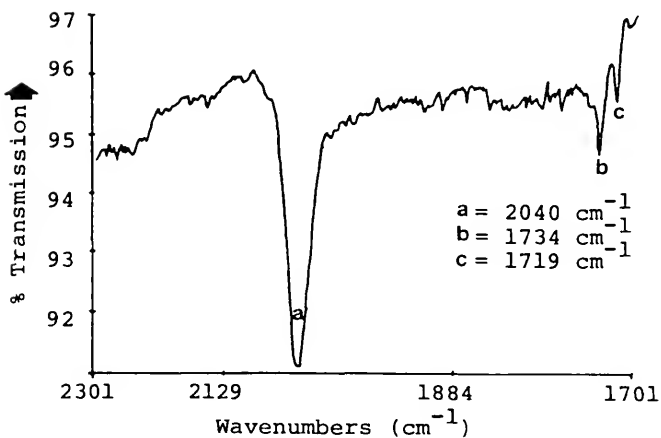


Figure 3-15. Infrared Spectra for the Supported Clusters After Exposure to the Reactant Gases at 75°C A) High Load System B) Low Load System

loading), the predominant absorption observed in the infrared spectrum was at  $2040\text{ cm}^{-1}$ . If the iridium weight percentage was above approximately 2.00% (high loading), the predominant absorption observed in the infrared spectrum was at  $2069\text{ cm}^{-1}$ . It also was found that an infrared spectrum containing both the absorptions at  $2069$  and  $2040\text{ cm}^{-1}$  could be obtained at  $75^\circ\text{C}$  for supported clusters containing between 1-2% iridium by weight. Since similar infrared spectra were obtained for the various supported clusters after exposure to the reactant gases, it is suggested that the clusters are converted into the same active species or precursor to the active species. Therefore, all of the supported clusters are expected to exhibit similar activity towards carbon monoxide reduction.

Infrared absorptions at  $1734$  and  $1719\text{ cm}^{-1}$  as shown in Figure 3-15 were observed in the spectra obtained for the activated clusters at  $75^\circ\text{C}$ . These absorptions are more noticeable in the infrared spectra of the supported systems containing a lower weight percentage of iridium. Since these infrared absorptions suggest the presence of bridging carbonyl ligands, it is possible that multinuclear iridium carbonyl species are still present in the activated systems at  $75^\circ\text{C}$ .

A change in the infrared spectra as shown in Figure 3-16 was observed upon raising the temperature in the high and low iridium loaded systems. A shifting of the infrared

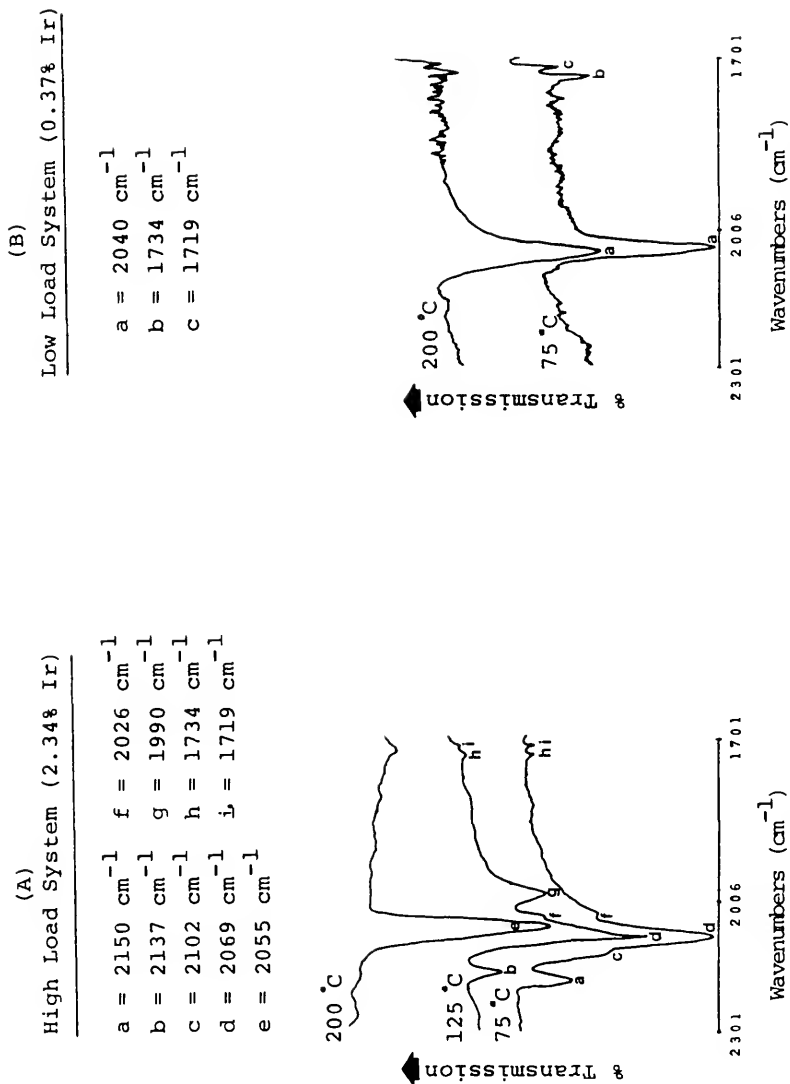


Figure 3-16. Infrared Spectra Obtained for the Low and High Load Iridium Systems at Various Temperatures (A) High Load System (B) Low Load System

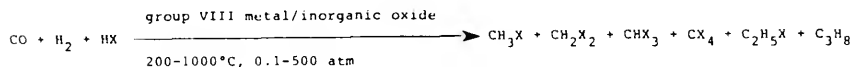
absorption at  $2150\text{ cm}^{-1}$  to  $2137\text{ cm}^{-1}$  and a decrease in the intensity of the bridging carbonyl absorptions at  $1734$  and  $1719\text{ cm}^{-1}$  were observed for the high load iridium system upon raising the temperature from  $75^{\circ}\text{C}$  to  $125^{\circ}\text{C}$ . At temperatures exceeding  $200^{\circ}\text{C}$ , the infrared spectrum for this system exhibited only one absorption at  $2055\text{ cm}^{-1}$ . The infrared spectrum for the low load iridium system upon raising the temperature above  $200^{\circ}\text{C}$  showed the disappearance of the bridging carbonyl absorptions and a broadening in the primary absorption at  $2040\text{ cm}^{-1}$ . Since the infrared spectra for the high and low load iridium systems change upon raising the temperature, it is suggested that further decomposition of the iridium species occurs at these elevated temperatures.

#### Verification That A Discrete Molecule Complex Exists in the Activated Iridium Systems

It is evident from the change that has occurred in the infrared spectra upon raising the temperature that the supported clusters are being converted to either another iridium carbonyl complex or to a carbonylated iridium metal surface. Vannice has reported that halogenated hydrocarbons can be produced from synthesis gas and  $\text{HCl(g)}$  over inorganic oxide supported iridium metal as shown in Equation 3-19.<sup>194</sup>

It should be noted that this reaction is claimed to occur between the temperature range of  $200\text{--}1000^{\circ}\text{C}$ . It also has been reported that methyl chloride is temporarily observed during the conversion of synthesis gas to

hydrocarbons at 250°C over iridium metal supported on an inorganic oxide support.<sup>195</sup> The chloride content was found to originate from the initial impregnation of the support with  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  followed by its thermal deposition. It has



(3-19)

been reported that the phosphine substituted tetrairidium carbonyl clusters supported on inorganic oxides decompose to iridium metal above 180°C under an atmosphere of carbon monoxide and hydrogen.<sup>151</sup> Similarly,  $\text{Ir}_4(\text{CO})_{12}$  physisorbed on an inorganic oxide support has been shown to begin to decompose by CO dissociation between 50-350°C.<sup>196</sup> Furthermore, the predominant infrared absorption assigned for carbon monoxide absorption onto an iridium metal surface has been reported to range from 2010  $\text{cm}^{-1}$  at low metal coverage to 2093  $\text{cm}^{-1}$  at metal saturation.<sup>197-199</sup> Since the location of this broad infrared absorption has been reported to be influenced by a variety of parameters, such as the extent of metal loading<sup>197-199</sup>, the metal particle size<sup>122</sup>, the strength of the support interaction<sup>200</sup>, the oxidation state of the iridium metal<sup>200-202</sup> and the

temperature of the system<sup>201</sup>, it is possible that the changes observed to occur in the infrared spectra of the supported clusters upon exposure to the reactant gases (Figure 3-15) and an increase in reaction temperature (Figure 3-16) could be explained by the formation of metallic iridium.

Several control reactions using metallic iridium adsorbed onto an inorganic oxide support were run in order to ascertain if metallic iridium could account for the formation of the methyl chloride observed at 75°C in the supported cluster systems. Either  $\text{Ir}_4(\text{CO})_{12}$  or  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was physically adsorbed onto alumina to give supports containing 1.69% Ir and 2.30% Ir, respectively. Each sample was pretreated by calcination at 250°C under hydrogen for at least five hours. The resulting gray supports showed the formation of only a trace amount of methyl chloride at 75°C under  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$ . The formation of this methyl chloride at 75°C was observable only upon using a stagnant reactor. An increase in activity into the range of  $8.9 \times 10^{-12}$  -  $2.6 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  was observed for these metallic iridium systems upon raising the reaction temperature to 200°C. Deactivation of these metallic iridium systems was observed to occur upon exposure to air. This is not surprising since it has been reported that metallic iridium upon exposure to air undergoes oxidation and agglomeration to large crystallites of  $\text{IrO}_2$ .<sup>197,203</sup> The infrared spectra observed for these activated metallic

iridium systems contained one broad, weak absorption as shown in Figure 3-17. The location of this absorption was found to depend upon the extent of the metal loading. It is suggested from the interpretation of these results that the formation of metallic iridium in the supported iridium cluster systems cannot account for the observed activity of  $1.9 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  at  $75^\circ\text{C}$ .

In order to substantiate the existence of a discrete molecular complex in the activated supported cluster systems at  $75^\circ\text{C}$  samples of these systems taken prior to and after exposure to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$  were examined by x-ray photoelectron spectroscopy (ESCA). No change in the binding energy of the iridium core electrons as shown in Figure 3-18 was observed for analysis of the supported cluster (2.34% Ir) before and after activation. This suggests that the iridium species present after activation is a discrete molecular complex. This is further supported by a similar conclusion reported by Dow Chemical Company in an independent analysis of the supported iridium cluster by x-ray photoelectron spectroscopy.<sup>162</sup> The increased width of the signal in the iridium photoelectron spectrum as compared to molecular standards suggests that the iridium may be in several oxidation states.

The activity of the supported phosphine substituted tetrairidium carbonyl clusters towards the formation of methyl chloride was monitored over the temperature range of  $75\text{--}300^\circ\text{C}$  in order to determine if the temperature of the



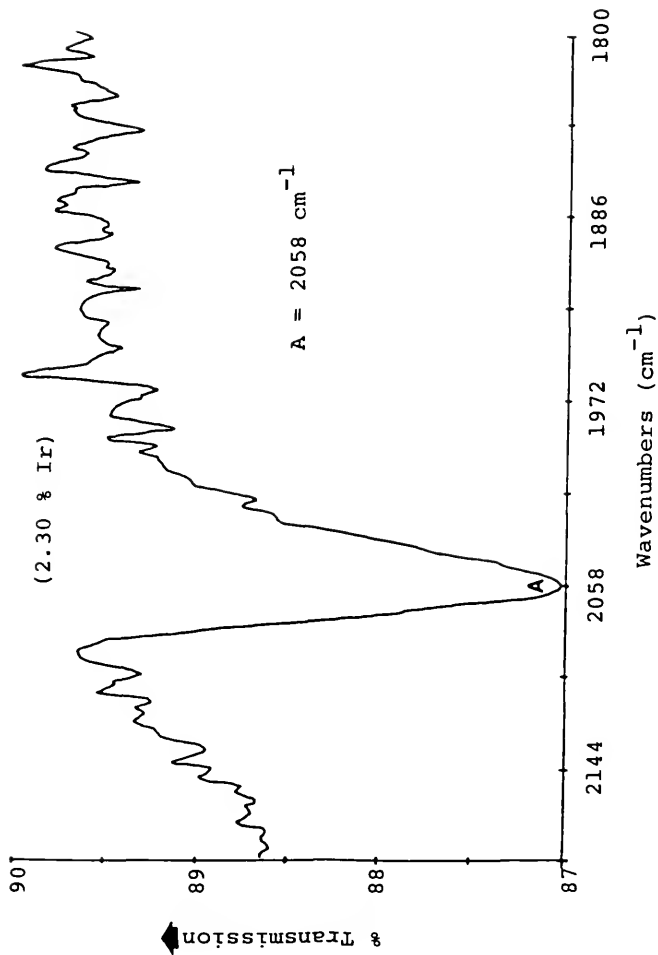


Figure 3-17. Infrared Spectrum Obtained for Metallic Iridium/Alumina After Exposure to CO, H<sub>2</sub> and HCl(g) at 200 °C

A = initial supported cluster  
(2.34% Ir)

B = Supported cluster (2.34% Ir)  
exposed to CO/H<sub>2</sub>/HCl at 100°C

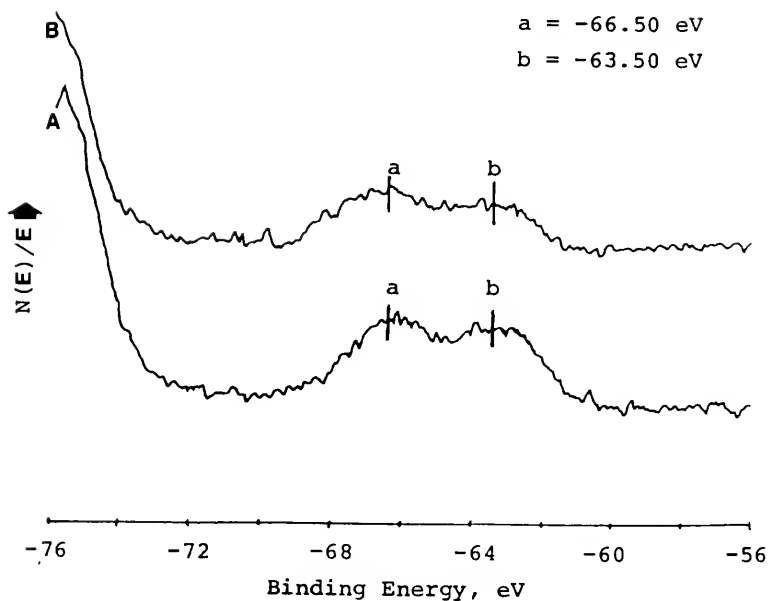
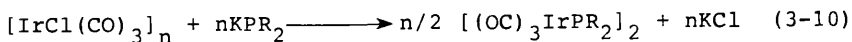


Figure 3-18. X-ray Photoelectron Spectrum for the Supported Clusters Before and After Activation

system would have any effect on the formation of metallic iridium. The activity at 75°C was observed to average  $3.27 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$ . A decrease in activity to  $9.20 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  was observed between the temperature range of 125-200°C. The activity increased to  $4.23 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  upon raising the temperature above 200°C. It is proposed that between 75-125°C under  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$  the supported clusters decompose to form other discrete iridium complexes. The decrease in activity observed between 125-200°C can be explained by the gradual decomposition of these discrete iridium complexes to the less active metallic iridium. At temperatures exceeding 200°C most of the discrete iridium complexes are decomposed to metallic iridium. The activity of the system between 200-300°C was observed to increase because the metallic iridium becomes more active towards the formation of methyl chloride in this temperature range.<sup>194</sup>

Investigation by Infrared Spectroscopy of the Discrete Iridium Species Present in the Activated Systems at 75°C

Collman et al. proposed that  $\text{IrCl(CO)}_3$  was either the active catalyst or catalyst precursor for carbon monoxide conversion in the homogeneous  $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$  melt system.<sup>141</sup> It also has been reported that  $[\text{IrCl(CO)}_3]_n$  will react with a phosphine substituent to form dinuclear iridium complexes as shown in Equation 3-10.<sup>204</sup> A supported iridium



carbonyl complex was prepared by reacting  $\text{IrCl}(\text{CO})_3$  with a phosphinated support in refluxing toluene. The infrared spectrum for this supported iridium complex is very similar to that obtained at  $75^\circ\text{C}$  for the activated supported iridium clusters containing a low iridium content as shown in Figure 3-19. The presence of the bridging carbonyl absorptions at 1734 and  $1719\text{ cm}^{-1}$  indicates that the reaction between  $\text{IrCl}(\text{CO})_3$  and the phosphinated support yields a multinuclear iridium species. Unfortunately, the supported iridium carbonyl complex responsible for the infrared absorptions at 2045(vs), 1990(shoulder), 1734(m) and  $1719\text{ (w) cm}^{-1}$  as shown in Figure 3-19 has not been identified. There is only limited data available in the literature concerning the characterization of multinuclear phosphine substituted iridium clusters which contain bridging carbonyls and possibly chlorine ligands.<sup>151,158,189,205,206</sup> The only iridium complex that was found in the literature to give rise to an infrared spectrum which is similar to the observed infrared spectrum (Figure 3-19) is the multinuclear species,  $[\text{Ir}_2(\text{CO})_4\text{Cl}((\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2)_2][\text{BPh}_4]$ .<sup>206</sup> The supported multinuclear iridium species prepared from the reaction of  $\text{IrCl}(\text{CO})_3$  with the phosphinated support was exposed to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$  at  $75^\circ\text{C}$ . The activity of this supported complex at  $75^\circ\text{C}$  for the formation of methyl chloride was observed to be  $9.10 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$ . A change in the infrared spectrum of this supported iridium complex, as shown in Figure 3-20, was observed to

A = Initial  $\text{IrCl}(\text{CO})_3/\text{PPh}_2$  containing 1.66% Ir

B = Supported cluster (Low Load - 0.37% Ir) exposed to  $\text{CO}/\text{H}_2/\text{HCl}$  at  $75^\circ\text{C}$

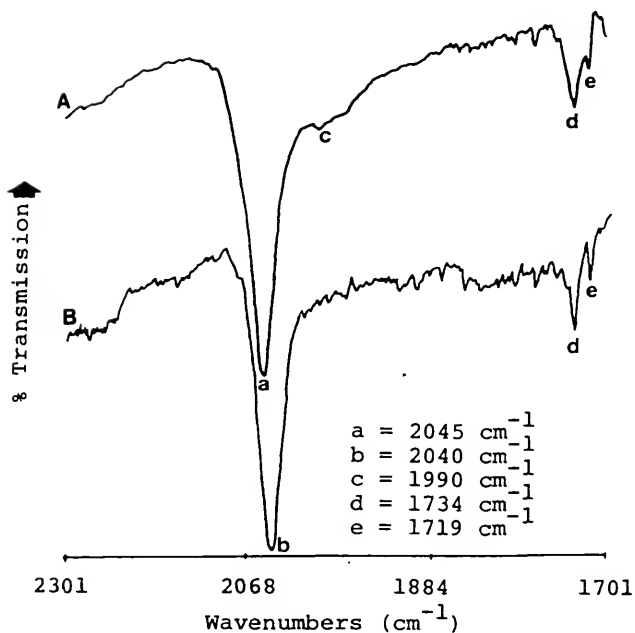


Figure 3-19. A Comparison of the Infrared Spectra Obtained for the Supported Clusters (Low % Ir) and for  $\text{IrCl}(\text{CO})_3$  on a Phosphinated Support

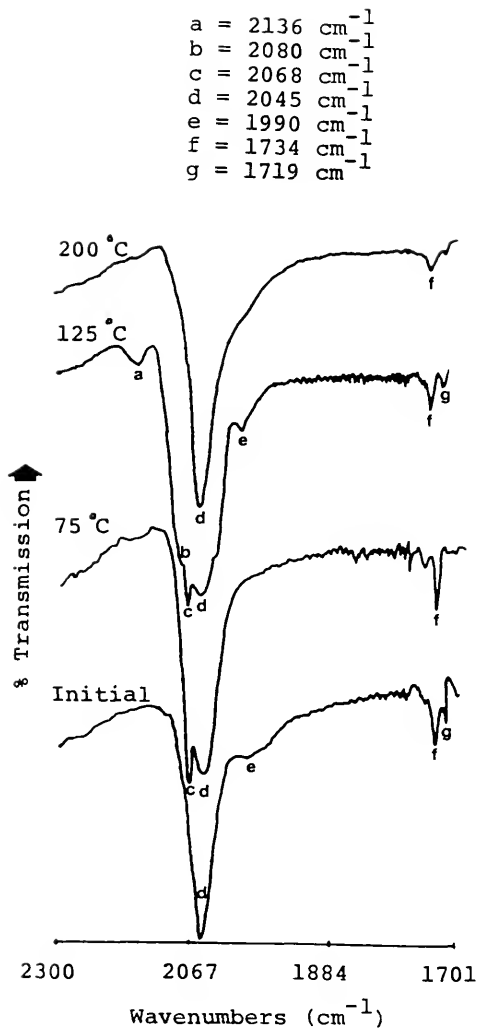
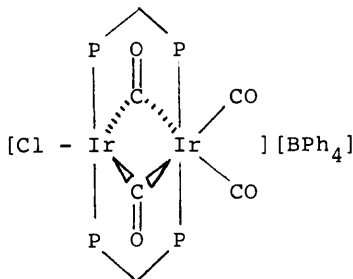


Figure 3-20. Infrared Spectrum of  $\text{IrCl}(\text{CO})_3 + 3\text{-PPh}_2$  at Various Temperatures

occur after exposure to CO, H<sub>2</sub> and HCl(g) at various temperatures. At 75°C the growth of an infrared absorption at 2068 cm<sup>-1</sup> was observed to coincide with the disappearance of the shoulder at 1990 cm<sup>-1</sup>. The reappearance of this



2047(m), 1998(vs), 1759(s) cm<sup>-1</sup>

shoulder along with a shoulder at 2080 cm<sup>-1</sup> and a new absorption at 2136 cm<sup>-1</sup> was observed at 125°C. The primary infrared absorption at 200°C was observed to be a broad band at 2045 cm<sup>-1</sup>. In general, the intensity of the bridging carbonyl absorptions at 1734 and 1719 cm<sup>-1</sup> was observed to decrease as the reaction temperature was increased. The infrared spectrum taken after the supported complex had been activated at 125°C was observed to resemble the spectra obtained for the supported clusters containing a high iridium content (Figure 3-16) and for IrCl(CO)<sub>3</sub> (Figure 3-21).

A sample of IrCl(CO)<sub>3</sub> physically adsorbed onto alumina gave rise to an infrared spectrum that is similar to that obtained for the unsupported IrCl(CO)<sub>3</sub>. This spectrum also

is very similar to that observed at 75°-125°C for the supported clusters containing a high iridium content as shown in Figure 3-21. A change in the infrared spectrum as shown in Figure 3-22 was observed upon exposing the  $\text{IrCl}(\text{CO})_3$  adsorbed on alumina to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  at various temperatures. Primarily, the growth of a new absorption at  $2109\text{ cm}^{-1}$  and the splitting of the  $2142\text{ cm}^{-1}$  absorption into two absorptions at  $2154$  and  $2139\text{ cm}^{-1}$  was observed at 75°C. This change which has occurred in the infrared spectrum of  $\text{IrCl}(\text{CO})_3$  on alumina at 75°C is suggested to be caused by the formation of different isomers of  $[\text{IrCl}(\text{CO})_3]_n$ . The infrared spectrum at 200°C for the activated  $\text{IrCl}(\text{CO})_3/\text{alumina}$  exhibited only a broad absorption at  $2073\text{ cm}^{-1}$ . The formation of only a trace amount of methyl chloride ( $<10^{-14}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$  accumulated in a stagnant reactor for twelve hours) was observed for this system at 75°C. The formation of this trace amount of methyl chloride most likely occurs through the previously discussed minor impurity routes. The activity of the system was observed to increase to  $6.30 \times 10^{-12}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$  at 200°C.

The infrared and activity data obtained for  $\text{IrCl}(\text{CO})_3$  adsorbed on alumina and supported on phosphinated alumina parallels the results obtained for the supported clusters at various temperatures. It is proposed that the active species present in the supported cluster systems is a multinuclear iridium species characterized by infrared



A = Supported cluster (high load - 2.34% Ir)  
at 125 °C

B = Supported cluster (high load - 2.34% Ir)  
at 75 °C

C =  $\text{IrCl}(\text{CO})_3$

D =  $\text{IrCl}(\text{CO})_3$  / Alumina (1.40% Ir)

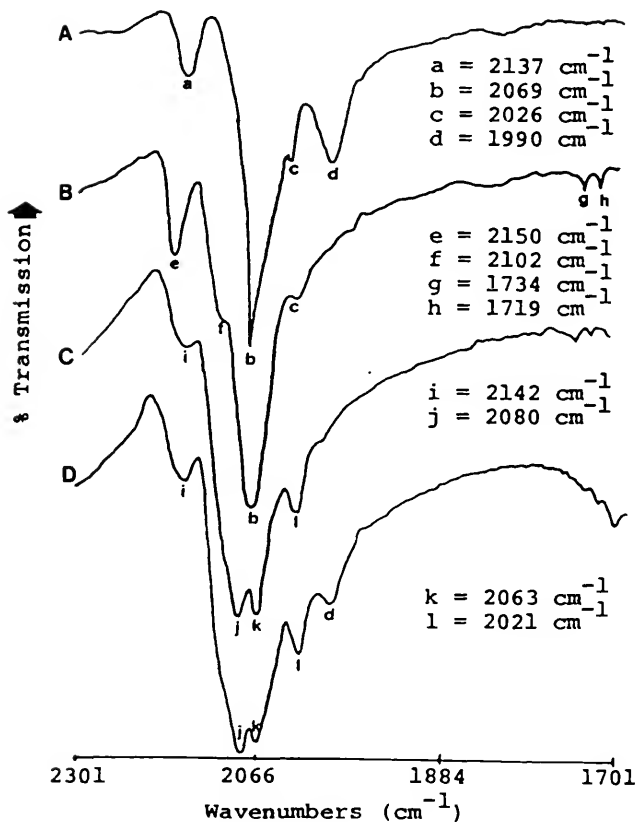


Figure 3-21. A Comparison of the Infrared Spectrum of  $\text{IrCl}(\text{CO})_3$ /Alumina With the Spectra Obtained for the Activated Iridium Clusters at Various Temperatures

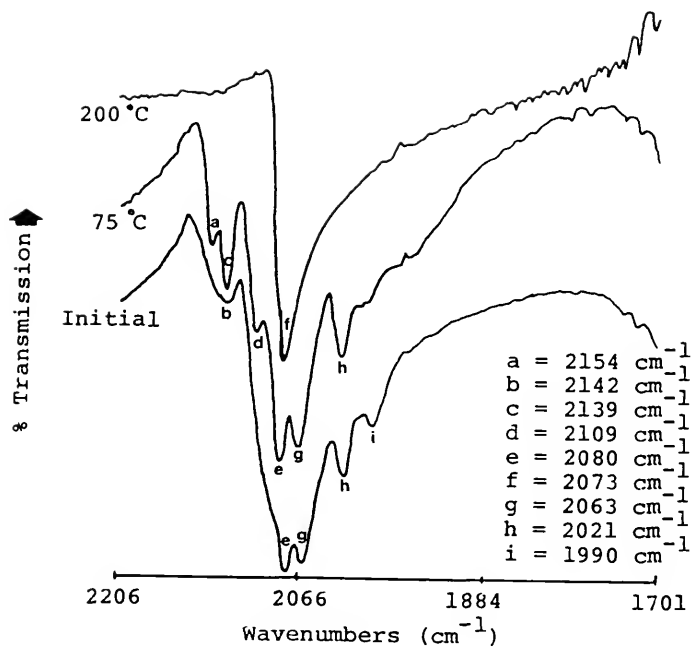


Figure 3-22. Infrared Spectrum of  $\text{IrCl}(\text{CO})_3/\text{Alumina}$  at Various Temperatures

absorptions at 2045, 1734 and 1719  $\text{cm}^{-1}$  as shown in the infrared spectrum (Figure 3-19) of the activated supported cluster containing a low iridium content. Similar infrared absorptions (Figure 3-19) and activity was observed for the  $\text{IrCl}(\text{CO})_3$  supported on phosphinated alumina. The presence of this multinuclear species also is indicated in the infrared spectrum (Figure 3-15) of the supported clusters containing a high iridium content by the presence of weak absorptions at 1734 and 1719  $\text{cm}^{-1}$ . Thus, the presence of this multinuclear species can explain the similarity observed in the activity of the supported cluster systems containing either a high or low iridium content. This proposal is further supported by the observed inactivity of the  $\text{IrCl}(\text{CO})_3/\text{alumina}$  system along with the absence of any bridging carbonyl absorptions in the corresponding infrared spectrum (Figure 3-22). Final support for this proposal arises from the exchange of  $^{13}\text{CO}$  for  $^{12}\text{CO}$  in this multinuclear iridium complex as shown in the infrared data portrayed in Figure 3-23.

It is proposed that this active multinuclear complex is gradually decomposed to  $\text{IrCl}(\text{CO})_3$  under the reaction conditions. The rate of this decomposition is increased as the temperature of the system is raised. This proposal is based on the temperature induced growth of the infrared absorptions in the infrared spectrum (Figure 3-20) of the active multinuclear complex which are similar to those of  $\text{IrCl}(\text{CO})_3$  (Figure 3-21). It also is suggested that the

A = Sample exposed to  $^{12}\text{CO}/\text{H}_2/\text{HCl}$  at  $75^\circ\text{C}$

B = Sample exposed to  $^{13}\text{CO}/\text{H}_2/\text{HCl}$  at  $75^\circ\text{C}$

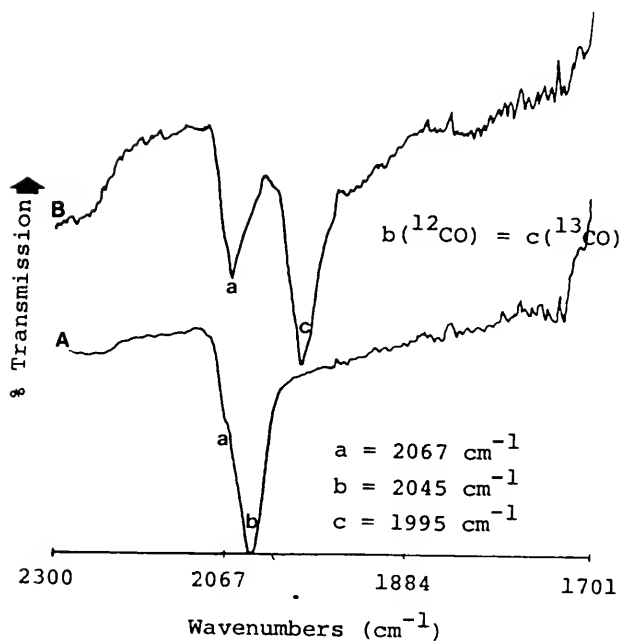


Figure 3-23. Infrared Spectrum of a Mixture of the Supported Multinuclear Complex and  $\text{IrCl}(\text{CO})_3$  Exposed to Carbon-13 Carbon Monoxide

$\text{IrCl}(\text{CO})_3$  is inactive towards the formation of methyl chloride. This is supported by the inactivity of the  $\text{IrCl}(\text{CO})_3$ /alumina system. Further support arises from the inability to substitute  $^{13}\text{CO}$  for the carbon-12 carbonyl absorption at  $2067\text{ cm}^{-1}$  assigned to  $\text{IrCl}(\text{CO})_3$  in the infrared spectrum shown in Figure 3-23. As the temperature of the supported cluster systems is increased, the decrease in observed activity is caused by the formation of  $\text{IrCl}(\text{CO})_3$  and iridium metal. The formation of iridium metal is completed at temperatures above  $200^\circ\text{C}$ . The increase in the system's activity observed above  $200^\circ\text{C}$  previously has been described by Vannice.<sup>194</sup>

In order to ascertain if similar results could be obtained from other supported iridium carbonyl complexes, Vaska's complex,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , was reacted in refluxing toluene with a phosphinated support. The supported complex was characterized by infrared spectroscopy to contain a mixture of products as shown in Figure 3-24. The carbonyl infrared absorption at  $1965\text{ cm}^{-1}$  can be assigned to the carbonyl ligand in  $\text{Ir}-(\text{PPh}_2)_2\text{Ir}(\text{CO})\text{Cl}$ . The remaining infrared absorptions at 2041, 2014, 1734 and  $1719\text{ cm}^{-1}$  resemble those previously assigned to a multinuclear iridium complex. An activity of  $1.38 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$  was observed at  $75^\circ\text{C}$  for this supported complex. The infrared spectrum of this supported complex (Figure 3-24) exposed to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  at  $75^\circ\text{C}$  showed the disappearance of the  $1965$  and  $2014\text{ cm}^{-1}$  absorptions and the

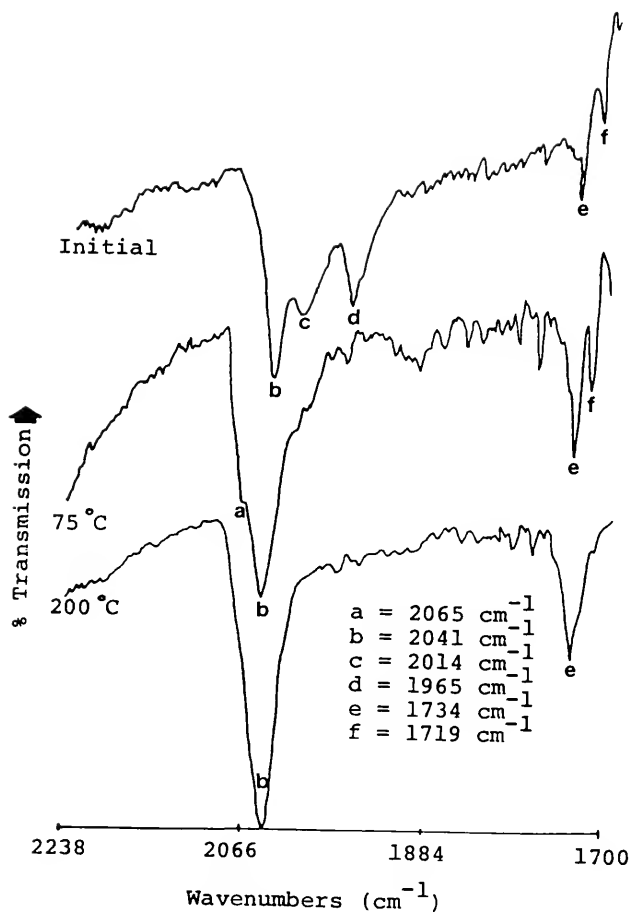


Figure 3-24. Infrared Spectrum of Vaska's Complex Supported on Alumina After Exposure to  $\text{CO}/\text{H}_2/\text{HCl}(\text{g})$  at Various Temperatures

growth of a shoulder at  $2065\text{ cm}^{-1}$ . This shoulder at  $2065\text{ cm}^{-1}$  is suggested to be due to the formation of  $\text{IrCl}(\text{CO})_3$ . Above  $200^\circ\text{C}$ , the predominant infrared absorption was observed to be a broad absorption centered at  $2041\text{ cm}^{-1}$ . Thus it has been shown that Vaska's complex,  $\text{IrCl}(\text{CO})_3$  and  $\text{Ir}_4(\text{CO})_{12}$  supported on a phosphinated inorganic oxide support behave in a similar fashion under identical reaction conditions.

#### Reevaluation of the Supported Cluster/ $\text{AlCl}_3$ -NaCl System

Since all early work involving the  $\text{AlCl}_3$ -NaCl melt solvent was performed in the presence of residual 2-methoxyethanol, it was decided worthwhile to reevaluate the previously reported results.<sup>148</sup> The supported iridium clusters made in the absence of 2-methoxyethanol were tested in  $\text{AlCl}_3$ -NaCl under similar conditions to those previously reported.<sup>148</sup> At  $25^\circ\text{C}$ , the formation of a trace amount of methyl chloride was observed in a stagnant reactor. The activity was found to increase at  $50^\circ\text{C}$  to  $3.97 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$  and at  $75^\circ\text{C}$  to  $4.76 \times 10^{-11}$  moles  $\text{CH}_3\text{Cl sec}^{-1}\text{ g}^{-1}$ . Allowing the reaction to proceed at  $75^\circ\text{C}$  for several hours caused partial melting of the  $\text{AlCl}_3$ -NaCl salt. Control reactions of either  $\text{AlCl}_3$  or  $\text{AlCl}_3$ -NaCl run in this temperature range were observed not to be active for methyl chloride formation. An infrared spectrum as shown in Figure 3-25 of the activated supported iridium cluster in the  $\text{AlCl}_3$ -NaCl melt was observed to be similar to the reported spectrum (Table 3-2) obtained by Meutterties et al.<sup>140</sup> It

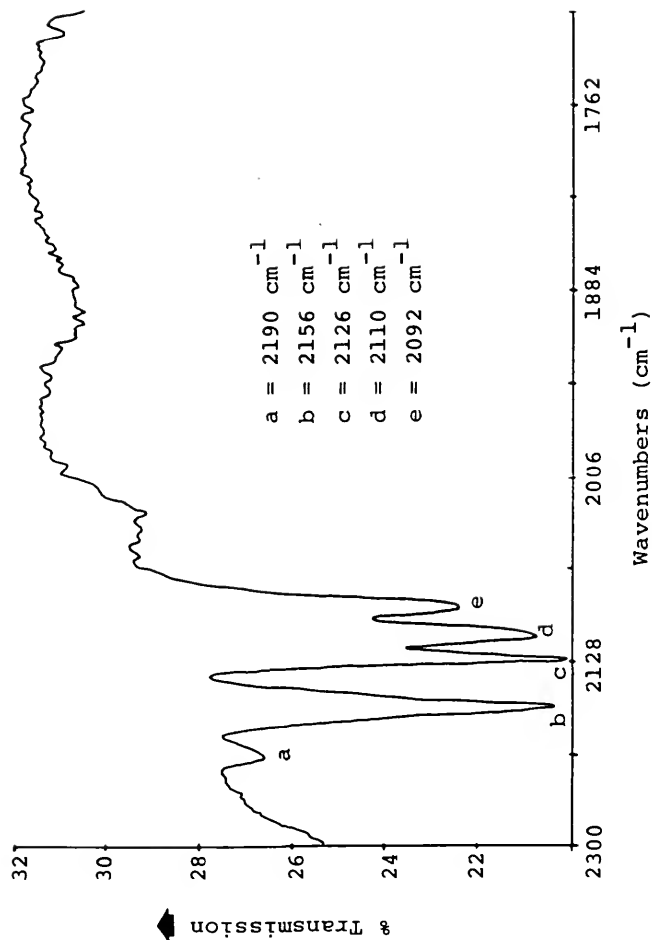


Figure 3-25. Infrared Spectrum of the Supported Iridium Clusters in an  $\text{AlCl}_3\text{-NaCl}$  Melt



should be noted that this infrared spectrum is completely different from those obtained for the supported clusters in the absence of the melt solvent. This indicates that the homogeneous system in the  $\text{AlCl}_3$ -NaCl melt solvent is different from the heterogeneous system employing  $\text{HCl(g)}$ . Finally, it was confirmed that leaching of the supported iridium complex into the melt solvent did occur under the reaction conditions. Therefore, the use of a supported iridium cluster in an  $\text{AlCl}_3$ -NaCl melt solvent has no inherent advantages over using a discrete homogeneous complex.

#### Proposed Mechanism for the Formation of Methyl Chloride

A mechanism for the formation of methyl chloride in the supported cluster systems can be divided into two separate sections. The first section, which pertains to the gradual degradation of the supported cluster and to the decomposition of impurities that are present in the system, is shown in Figure 3-26. Since  $^{13}\text{CO}$  studies have shown the incorporation of only 1.4% carbon-13 above natural abundance into methyl chloride, this cluster degradation and impurity decomposition pathway initially accounts for approximately 98% of the observed methyl chloride. However, it is predicted that as the reaction time progresses a greater percentage of the methyl chloride observed will arise from a second pathway involving the reduction of carbon monoxide.

The thermal decomposition of  $\text{Ir}_4(\text{CO})_{12}$  on an inorganic oxide support under an argon or carbon monoxide atmosphere

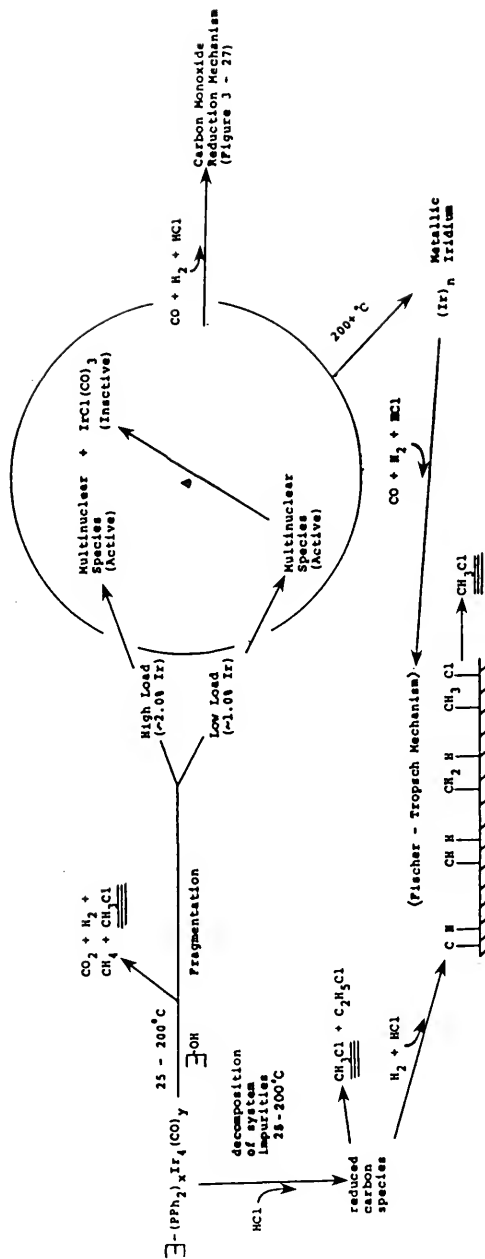
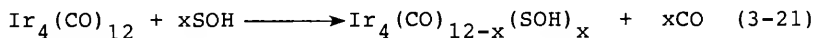


Figure 3-26. Proposed Mechanism for the Initial Formation of Methyl Chloride in the Supported Iridium Cluster System

has been reported to produce carbon dioxide, hydrogen and various hydrocarbon products.<sup>207,208</sup> The evidence suggests that the production of hydrogen arises from the interaction of the surface hydroxyl groups of the support with the tetrairidium carbonyl cluster. Therefore, the fragmentation of the adsorbed  $\text{Ir}_4(\text{CO})_{12}$  is initiated by the displacement of carbonyl ligands with surface hydroxyl groups as shown in Equation 3-21.<sup>208</sup> The formation of carbon dioxide and



hydrogen results from a water-gas shift type reaction involving carbon monoxide and either adsorbed water or the surface hydroxyl groups. Recall that the formation of carbon dioxide from the reaction involving the supported phosphine substituted tetrairidium carbonyl clusters was confirmed by GC/MS. The decomposition of the supported phosphine substituted iridium carbonyl clusters is most likely initiated through a similar interaction with the remaining hydroxyl groups of the support. It is suggested that the stabilization of the supported clusters may result from the silanation of the remaining hydroxyl groups with  $\text{Cl}_2\text{SiPPh}_2$  as shown in Equation 3-18 prior to exposure to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl(g)}$ .

If the concentration of the supported iridium cluster was low, the predominant fragmentation product was observed to be a phosphine bound multinuclear iridium complex

containing bridging carbonyl ligands. If the concentration of the supported iridium cluster was high, the fragmentation products were observed to be a mixture of the multinuclear species and a complex similar to  $\text{IrCl}(\text{CO})_3$ . It is suggested that this multinuclear species may be similar to the previously reported complex,  $[\text{Ir}_2(\text{CO})_4\text{Cl}((\text{Ph})_2\text{PCH}_2\text{P}-(\text{Ph})_2)_2][\text{BPh}_4]$ .<sup>206</sup> The conversion of this multinuclear complex into  $\text{IrCl}(\text{CO})_3$  was observed by infrared spectroscopy to occur as the reaction temperature was increased. However, raising the temperature above  $200^\circ\text{C}$  resulted in the formation of metallic iridium,  $(\text{Ir})_n$ , as evidenced by infrared spectroscopy and the resulting gray color of the supports. The formation of methyl chloride at temperatures above  $200^\circ\text{C}$  can be accounted for by a Fischer-Tropsch mechanism as previously described by Vannice.<sup>194</sup> Similarly, a Fischer-Tropsch mechanism may be vital for the formation of methyl chloride from the carbon substituents formed in the decomposition of inherent minor impurities in the system.

It is proposed that the formation of methyl chloride also may result through a second pathway involving the reduction of carbon monoxide. A mechanism for the formation of methyl chloride from synthesis gas and  $\text{HCl}(\text{g})$  at low temperatures ( $25\text{--}200^\circ\text{C}$ ) as shown in Figure 3-27 only can be speculated upon at this time. It is proposed that the multinuclear iridium species can activate either hydrogen or  $\text{HCl}(\text{g})$  to form a hydride species. It has been well

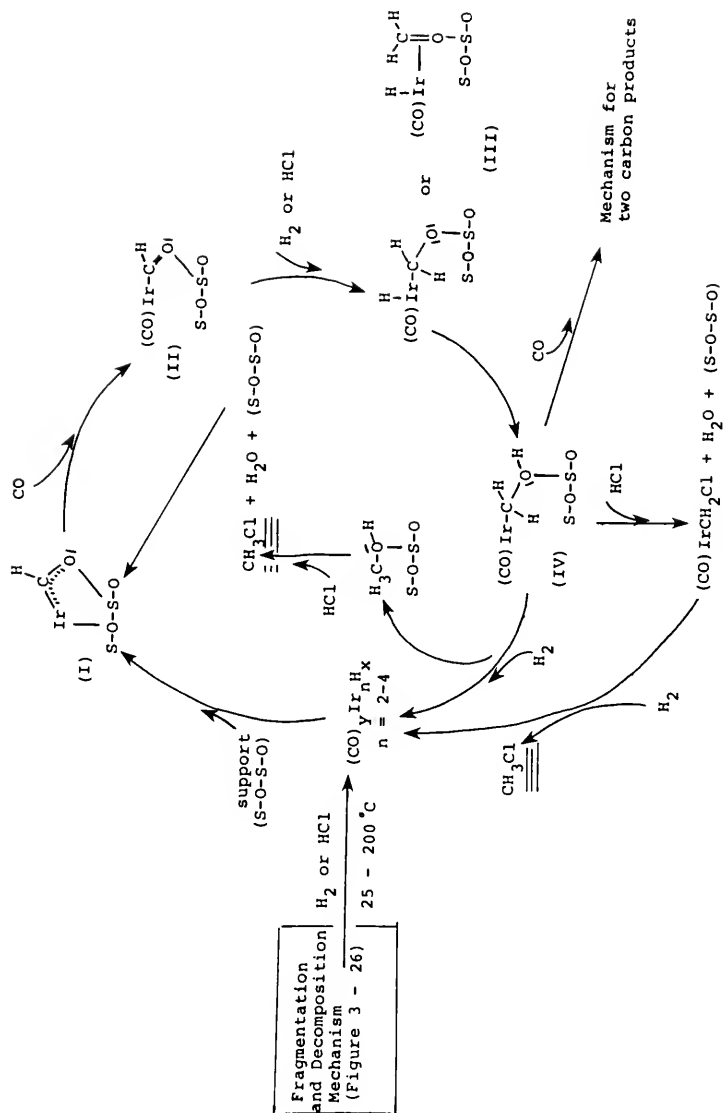
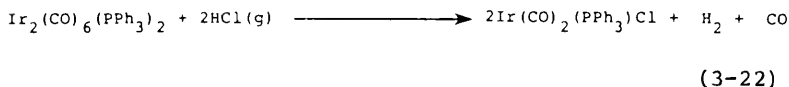


Figure 3-27. Proposed Mechanism for the Formation of Methyl Chloride from Synthesis Gas and  $\text{HCl(g)}$

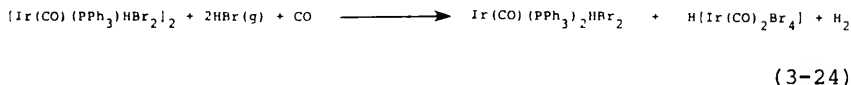
established that iridium carbonyl complexes can activate molecular hydrogen or hydrogen chloride to form hydride species.<sup>209-211</sup> For instance, the activation of hydrogen chloride by a dinuclear iridium complex has been reported<sup>211</sup> to result in the formation of a mononuclear complex as shown in Equation 3-22. The formation of another dinuclear iridium complex can result through the oxidative addition of



hydrogen or HCl as shown in Equation 3-23. The same reaction employing HBr in place of HCl leads to the stabilization of different iridium complexes.<sup>211</sup> Primarily, the presence of carbon monoxide induces the disproportionation of the dinuclear iridium species into mononuclear iridium complexes as shown in Equation 3-24. The formation of different iridium complexes from similar reactions employing HBr(g) or HCl(g) suggests the possibility that methyl halide formation from HBr(g) or HCl(g) may proceed

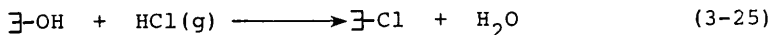


through the stabilization of different reaction intermediates. The formation of different discrete molecules could explain the inability of the iridium system



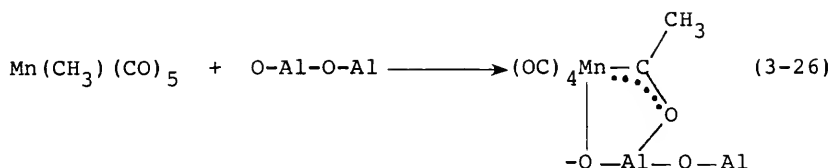
to reversibly utilize  $\text{HBr}(\text{g})$  and  $\text{HCl}(\text{g})$  to form the corresponding methyl halide as previously noted.<sup>148</sup>

The formation of an iridium hydride complex is most likely followed by hydride migration onto a carbonyl ligand. The formation of this formyl intermediate (I) is mediated through a bifunctional activation of the carbonyl ligand with an acidic site in the support. Hydride transfer to a carbonyl ligand previously has been reported to be facilitated in the presence of a Lewis acid.<sup>212</sup> It previously was proposed<sup>148</sup> that the  $\text{HCl}(\text{g})$  reacted with the support hydroxyl groups to form support-Cl moieties as shown in Equation 3-25. However, there have been several reports



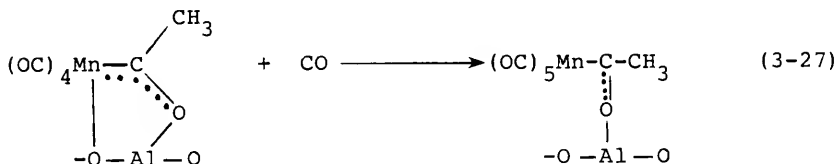
that indicate that this reaction does not occur in the temperature range of 25-500°C.<sup>213,214</sup> The hydride transfer to a carbonyl ligand most likely occurs in a similar fashion to the alkyl migration observed in the interaction of  $\text{Al}_2\text{O}_3$

with  $\text{Mn}(\text{CH}_3)(\text{CO})_5$  as shown in Equation 3-26.<sup>154</sup> In the presence of carbon monoxide the cyclic formyl



intermediate (I) can be rearranged to an acyclic formyl intermediate (II) by the addition of the carbon monoxide to the iridium center similar to that shown in Equation 3-27 for the  $\text{Mn}(\text{CH}_3)(\text{CO})_5/\text{alumina}$  system.<sup>154</sup>

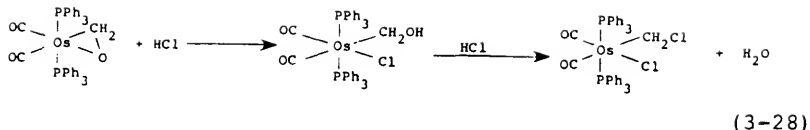
The subsequent addition of hydrogen to the acyclic formyl intermediate (II) could result in the formation of a bound formaldehyde type intermediate (III). Coleman et al. postulated the existence of a formaldehyde intermediate in the formation of the hydrocarbon products in the  $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3\text{-NaCl}$  system.<sup>141</sup> The formation of a bound formaldehyde intermediate in the homogeneous reduction of carbon monoxide to oxygenated products also has been proposed.<sup>134</sup> A bound formaldehyde complex can be





transformed into either a metal alkoxide complex,  $M-OCH_3$ , or a metal hydroxymethyl complex,  $M-CH_2OH$ . Since the bound formaldehyde complex (III) is stabilized by the interaction of a Lewis acid with the oxygen atom of the aldehyde, the most likely intermediate is the formation of the hydroxymethyl complex (IV). The formation of a hydroxymethyl intermediate should produce at least trace 2-carbon products due to migratory insertion of a carbonyl ligand into the Ir-C bond. This could account for some of the ethylene, acetaldehyde and ethyl chloride that was observed.

There are several ways in which methyl chloride can be formed from this hydroxymethyl intermediate (IV). First, the activation of hydrogen by the hydroxymethyl intermediate (IV) could rejuvenate the initial iridium hydride complex while forming methanol as a by-product. The methanol could react with  $HCl(g)$  over an inorganic oxide to form methyl chloride and water. It has been observed that in low concentrations methanol can be converted in 100% yields to methyl chloride under the reaction conditions employed. Secondly, the activation of  $HCl$  could lead to the formation of a chloromethyl iridium complex (V). Further activation of hydrogen could produce the observed methyl chloride and rejuvenate the initial iridium hydride complex. The formation of a chloromethyl osmium complex from the activation of  $HCl$  by a bound formaldehyde complex as shown in Equation 3-28 has been reported.<sup>215</sup> For continuity, the



overall mechanism including both subdivisions is shown in Figure 3-28. Similar types of mechanisms including formyl, formaldehyde and hydroxymethyl intermediates has been proposed for the formation of alcohols.<sup>216,217</sup>

#### Investigation of a Phosphine Substituted Triosmium Carbonyl System

Since methyl bromide has been reported to be produced in a homogeneous  $\text{Os}_3(\text{CO})_{12}/\text{BBr}_3$  system, the formation of methyl chloride was attempted using a supported phosphine substituted osmium carbonyl cluster. The supported cluster was identified by infrared spectroscopy to be the supported mono-phosphine substituted triosmium carbonyl cluster as shown in Table 3-10. Upon exposure to the reactant gas mixture, very little activity towards the formation of methyl chloride was observed at 75°C. A comparison of the infrared spectrum of the supported osmium cluster that had been exposed to the reactant gases at 75°C with the infrared spectrum of  $\text{Os}_3(\text{CO})_{12}$  as shown in Figure 3-29 indicates that  $\text{Os}_3(\text{CO})_{12}$  is being formed in the reaction. The formation of  $\text{Os}_3(\text{CO})_{12}$  most likely occurs through the substitution of the phosphine ligand by the carbon monoxide in the reactant gas.

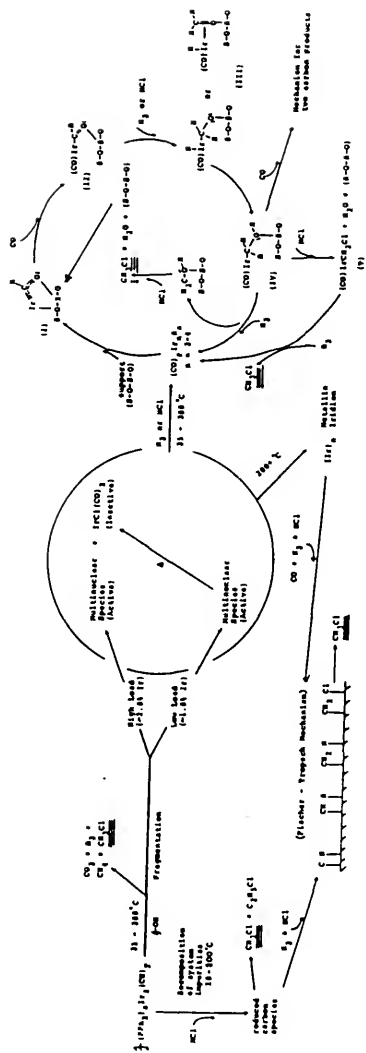


Figure 3-28. Overview of Proposed Mechanism for the Formation of Methyl Chloride in the Supported Iridium Cluster System

Table 3-10. Infrared Data for Complexes of Triosmium Carbonyl

Complex	Infrared Data (cm <sup>-1</sup> )	Environment	Reference
$\text{Al}(\text{C}_6\text{H}_5)_2\text{Os}_3(\text{CO})_{11}$	2103(w), 2079(w), 2074(w), 2066(m), 2050(m), 2039(s), 2023(vs), 1994(vs), 1986(m), 1966(s)	nujol	b(IV)
$\text{Si}(\text{C}_6\text{H}_5)_2\text{Os}_3(\text{CO})_{11}$	2107(m), 2054(s), 2035(s), 2019(vs), 2003(m), 1990(m), 1980(m)	nujol	218
$\text{Os}_3(\text{CO})_{12}$	2128(vw), 2067(s), 2060(s), 2040(m), 2027(m), 2015(m), 1995(m), 1983(m)	nujol	b (Fig. 3-28)
$\text{Os}_3(\text{CO})_{11}(\text{O}-\text{C}_6\text{H}_5)$	2117(m), 2080(vs), 2067(vs), 2033(vs), 2015(s), 1996(m)	pellet	219
$\text{H}_2\text{Os}_3(\text{CO})_{10}$	2110(vw), 2076(vs), 2062(s), 2025(vs), 2009(s), 1987(m), 1969(vw), 1956(vw)	pellet	220

b = This work; Al = Alumina; Si = Silica gel; (IV) = location of spectrum in appendix B; vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

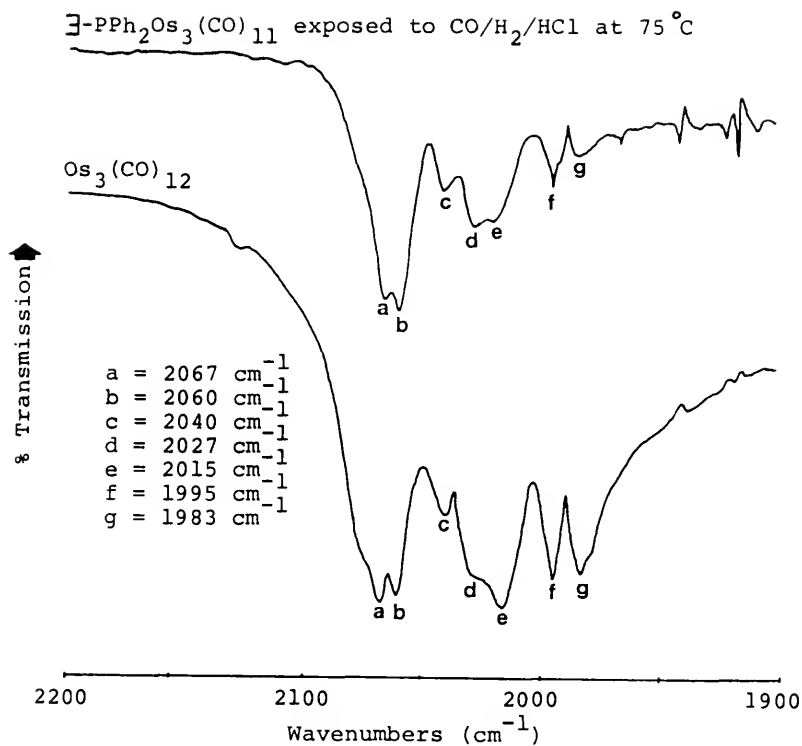
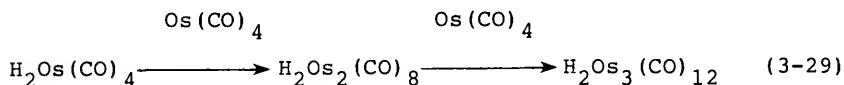


Figure 3-29. Comparison of the Infrared Spectrum of  $\exists$ -PPh<sub>2</sub>Os<sub>3</sub>(CO)<sub>11</sub> Exposed to CO, H<sub>2</sub> and HCl(g) With that of Os<sub>3</sub>(CO)<sub>12</sub>

It has been reported that  $\text{Os}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  physically adsorbed onto an inorganic oxide support decompose at  $200^\circ\text{C}$  through the formation of chemisorbed  $\text{Os}(\text{CO})_2$  and  $\text{Os}(\text{CO})_3$  fragments.<sup>220</sup> At lower temperatures, it is possible that an interaction between  $\text{Os}_3(\text{CO})_{12}$  and the hydroxyl groups on the support's surface could lead to the formation of a neutral hydrido cluster, such as  $\text{HOs}_3(\text{CO})_{10}^- (\text{O}-\text{E})$ .<sup>220</sup> Similar trinuclear osmium hydride complexes have been formed through the coupling of mononuclear species as shown in Equation 3-29.<sup>221</sup> Furthermore, it has been



reported that osmium hydride complexes, such as  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{11}$  react under carbon monoxide to yield  $\text{Os}_3(\text{CO})_{12}$ .<sup>221</sup> Therefore, it is not surprising that the formation of  $\text{Os}_3(\text{CO})_{12}$  was observed by infrared spectroscopy in the reaction of  $\text{H}_2$ , CO and  $\text{HCl}(\text{g})$  with the supported phosphine substituted triosmium carbonyl cluster at  $75^\circ\text{C}$ .

#### Investigation of Supported Cobalt and Iron Carbonyl Systems

A cost analysis of the various transition metals illustrates that the lower group VIII metals, such as iridium and osmium are the most expensive metals. Therefore, from an economic standpoint it would be

beneficial to utilize either cobalt or iron as catalysts for the commercial production of methyl chloride. For this reason,  $\text{Co}_2(\text{CO})_8$  was supported on a phosphinated support by a procedure similar to that reported by Evans et al.<sup>222</sup> Upon exposure to the reactant gases of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{HCl}(\text{g})$  at  $25^\circ\text{C}$  an immediate color change of white to blue was observed to occur. There was only a trace amount of methyl and ethyl chloride observed to be initially formed between  $75\text{--}100^\circ\text{C}$ . It is noted that this blue color is indicative of the formation of cobalt chloride. The formation of cobalt chloride is further supported in that the infrared spectrum of the supported cobalt carbonyl complex after exposure to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  did not show the presence of any carbonyl absorptions.

A supported phosphine substituted iron carbonyl complex was prepared by the thermal displacement of a carbonyl ligand in  $\text{Fe}(\text{CO})_5$  with a supported phosphine donor as reported by Wrighton et al.<sup>223</sup> This phosphine substitution reaction has been reported to be facilitated in the presence of a  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  catalyst.<sup>224</sup> The supported complex was characterized by infrared spectroscopy to be a mono-phosphine substituted iron tetracarbonyl complex as shown in Table 3-11. Upon exposure of the supported complex to the reactant gases at  $75^\circ\text{C}$  the formation of methyl and ethyl chloride was observed to occur at rates of  $4.56 \times 10^{-10}$  moles  $\text{CH}_3\text{Cl sec}^{-1} \text{ g}^{-1}$  and  $5.42 \times 10^{-10}$  moles  $\text{C}_2\text{H}_5\text{Cl sec}^{-1} \text{ g}^{-1}$ , respectively. This activity for the formation of

alkyl chlorides was observed to decrease rapidly with increasing reaction time. This deactivation process was

Table 3-11. Infrared Data for Supported Phosphine Carbonyl Complexes of Iron

<u>Complex</u>	<u>Infrared Data (cm<sup>-1</sup>)</u>	<u>Environment</u>	<u>Reference</u>
Al $\bar{\text{I}}$ -PPh <sub>2</sub> Fe(CO) <sub>4</sub>	2045(s), 1967(m), 1938(s)	nujol	b (Fig. 3-29)
Fe(CO) <sub>5</sub>	2025, 2000	isooctane	225
Fe(CO) <sub>4</sub> PPh <sub>3</sub>	2054, 1978, 1942	isooctane	225
(P)-PPh <sub>2</sub> Fe(CO) <sub>4</sub>	2045, 1968, 1932, 1876	KBr	225

b = This work; Al = Alumina; P = Polystyrene; s = strong,  
m = medium.

observed to be accompanied by a color change from tan to white in the support. The infrared spectrum of this white support did not exhibit any carbonyl absorptions as shown in Figure 3-30. The infrared absorption observed at 1595 cm<sup>-1</sup> corresponds to the C=C stretches in the phenyl groups of the phosphine linkage on the support. The absence of any carbonyl absorptions in the infrared spectrum suggests that under a carbon monoxide atmosphere the phosphine ligand in  $\bar{\text{I}}$ -PPh<sub>2</sub>Fe(CO)<sub>4</sub> is exchanged for a carbonyl group. The volatility of iron pentacarbonyl results in the metal complex being swept out of the system with the reactant and product gas stream. This is further supported in the discoloration that occurs in the gas lines and the mineral oil in the gas exhaust bubbler. Attempts to eliminate the



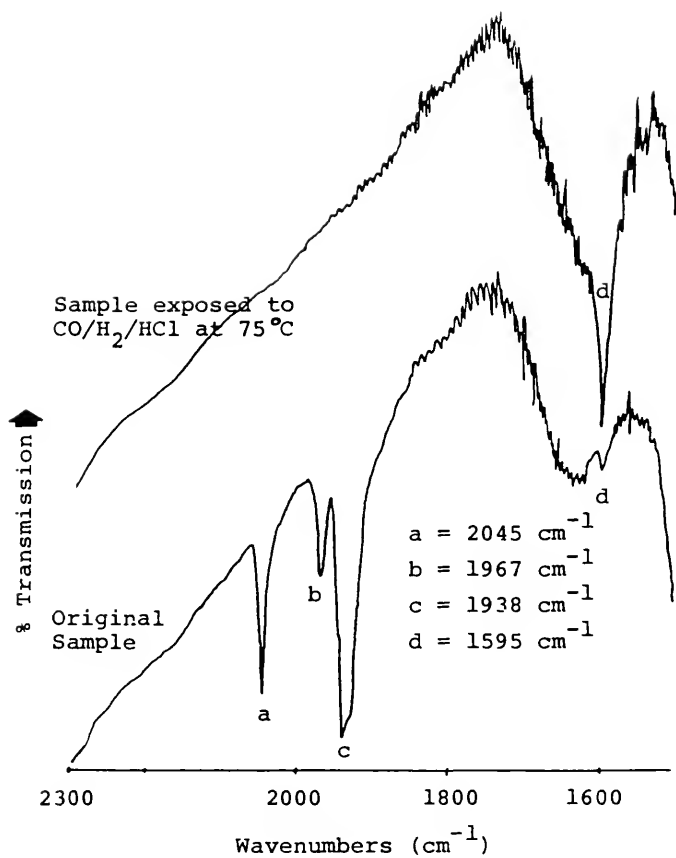


Figure 3-30. Infrared Spectrum of  $\text{Al}-\text{PPH}_2\text{Fe}(\text{CO})_4$  Before and After Exposure to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  at  $75^\circ\text{C}$

volatility problem of  $\text{Fe}(\text{CO})_5$  by initially supporting  $\text{Fe}_3(\text{CO})_{12}$  have been unsuccessful. It has been reported that nucleophilic attack on the iron cluster causes the degradation of the cluster into mononuclear carbonyl complexes.<sup>226</sup> The reaction of a phosphine donor with  $\text{Fe}_3(\text{CO})_{12}$  would proceed through metal-metal bond cleavage and result in the formation of  $\text{Al} \text{---} \text{PPh}_2\text{Fe}(\text{CO})_4$  units. Therefore, no advantage exists for supporting an iron cluster on a phosphinated support.

#### Investigation of a Phosphine Substituted Triruthenium Carbonyl System

A variety of other metal carbonyl complexes, such as  $\text{Re}_2(\text{CO})_{12}$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{Ru}_3(\text{CO})_{12}$  were supported on a phosphinated support through the substitution of a carbonyl ligand for a supported phosphine donor in refluxing benzene or toluene. In these trials the activity for methyl chloride production ranged from a trace amount for the rhodium and ruthenium complexes to an activity comparable to that observed for the supported iron complex for the manganese and rhenium complexes. It also was observed that a large amount of ethyl chloride and other two carbon products were formed in the reaction involving the supported ruthenium carbonyl complex. Gas chromatography and GC/MS identified the formation of methyl chloride, acetaldehyde, ethyl chloride, ethyl formate, diethyl ether, 1,1-dichloroethane, ethyl acetate and residual benzene solvent as shown in Figure 3-31. The mass spectra obtained

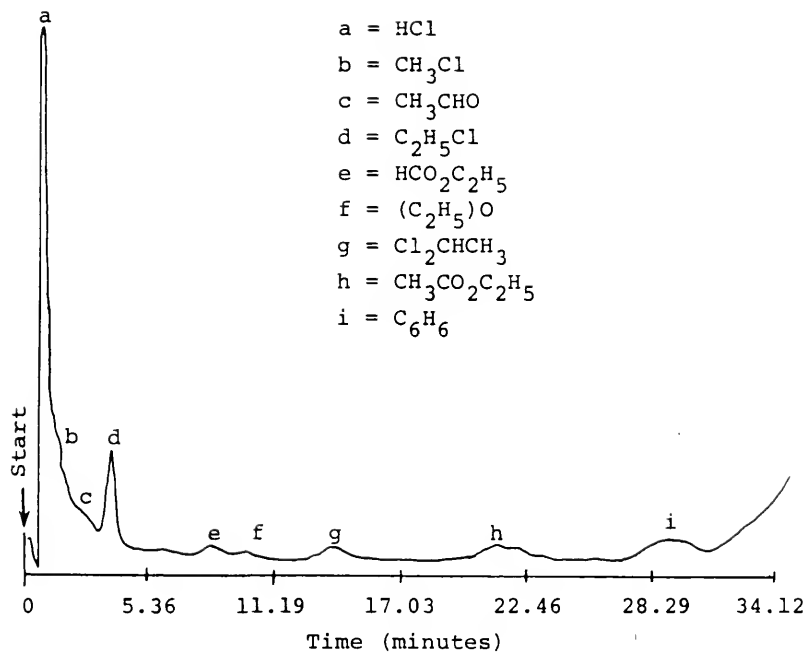


Figure 3-31. Gas Chromatogram of Two-Carbon Products Obtained in the Supported Ruthenium Cluster System

for these two carbon products are shown in Figures (3-32) - (3-37). The activity for the formation of ethyl chloride at 50°C using the supported ruthenium complex (1.01% Ru) was observed to be  $1.16 \times 10^{-9}$  moles  $C_2H_5Cl$   $sec^{-1} g^{-1}$ . If the  $HCl(g)$  content in the reactor feed gas was kept at a minimum, the formation of ethanol and methanol could be observed by gas chromatography. The supported ruthenium cluster is unique in that it is the only system that has shown a preference for the formation of two carbon products. This system also showed a much greater activity towards the formation of ethyl chloride than the supported iron, osmium, manganese, rhodium, rhenium or iridium systems. This contention is supported by a recently reported Ir-Ru/ $SiO_2$  catalyst system which showed an increase in CO conversion to  $C_2$ - $C_5$  hydrocarbons with an increase in the ruthenium content of the catalyst.<sup>227</sup> Unfortunately, carbon-13 labelling studies using  $^{13}CO$  have been inconclusive in ascertaining the extent of carbon-13 incorporation into ethyl chloride. However, these studies did show that 39% of the carbon dioxide observed was  $^{12}CO_2$ . This suggests that the supported ruthenium clusters are decomposing under the reaction conditions as did the supported iridium clusters.

The orange supported ruthenium complex was characterized by infrared spectroscopy to be a mixture of the mono-phosphine substituted triruthenium carbonyl cluster and  $Ru_3(\mu-H)(CO)_{10}(\mu-O-E)$ . It was found that by altering the concentration of  $Ru_3(CO)_{12}$  and the phosphine on the

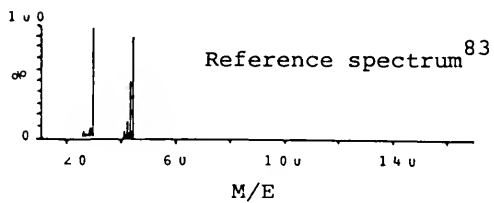
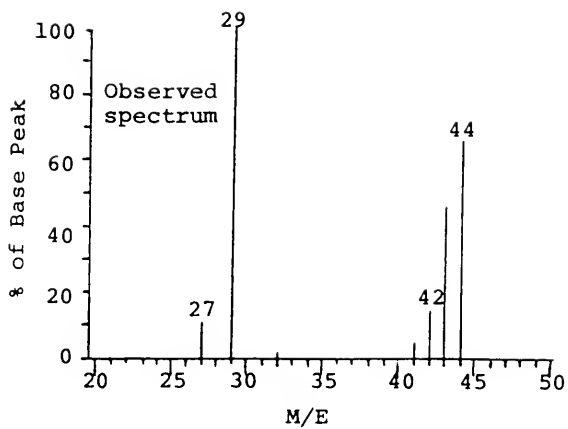


Figure 3-32. Mass Intensity Report for Acetaldehyde

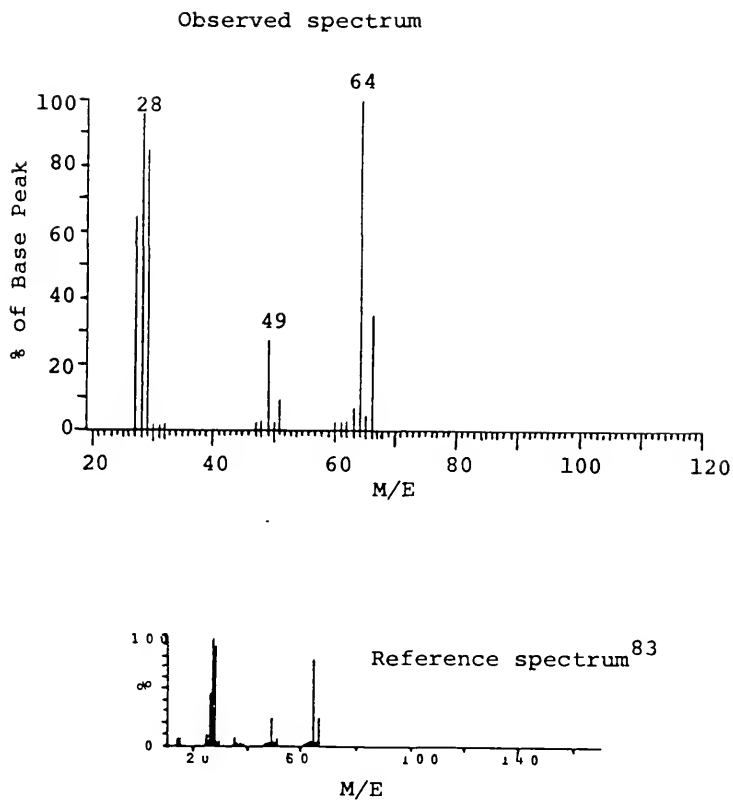


Figure 3-33. Mass Intensity Report for Ethyl Chloride

## Observed spectrum

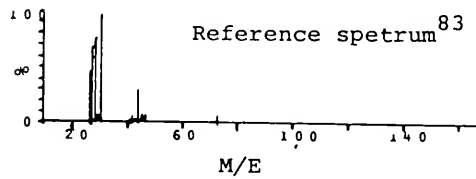
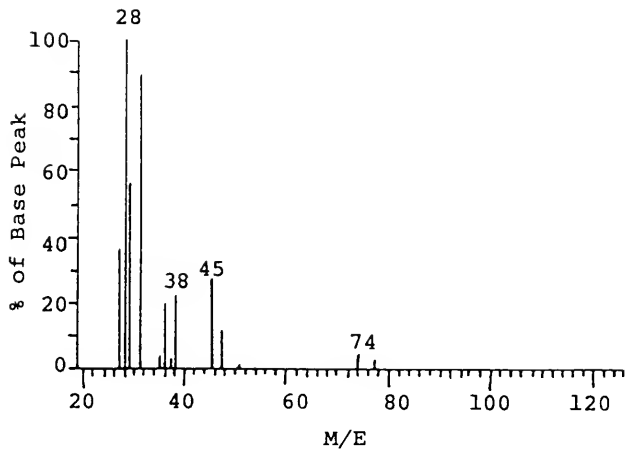


Figure 3-34. Mass Intensity Report for Ethyl Formate

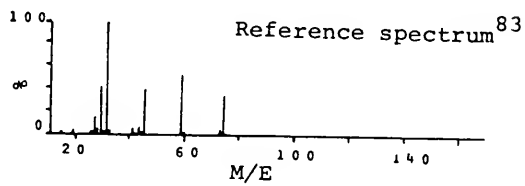
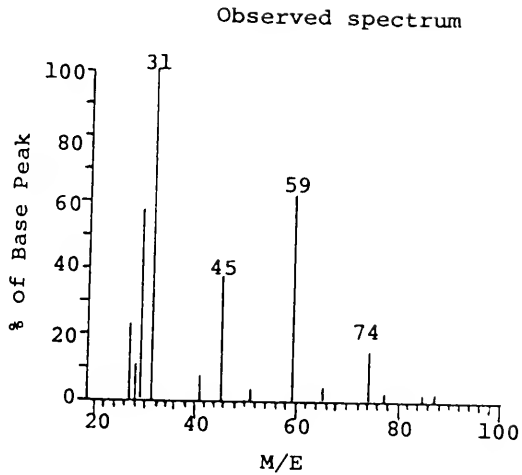


Figure 3-35. Mass Intensity Report for Diethyl Ether



## Observed spectrum

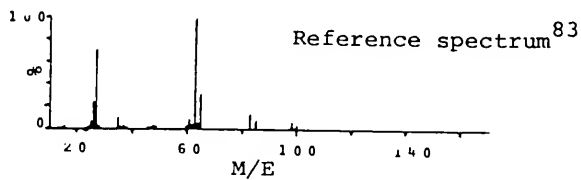
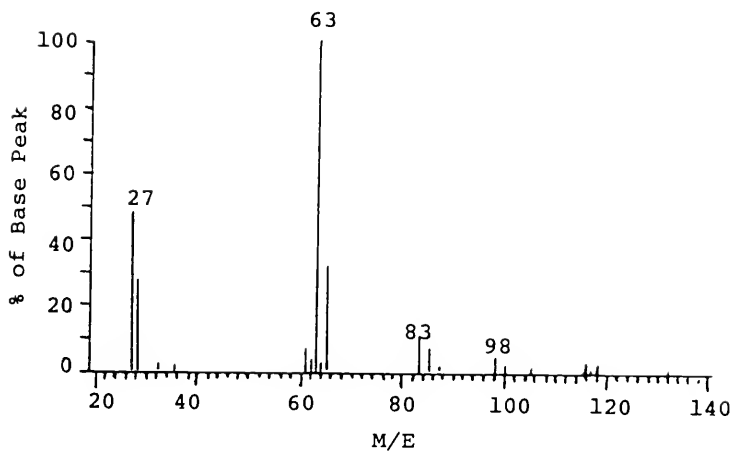


Figure 3-36. Mass Intensity Report for 1,1-Dichloroethane

## Observed spectrum

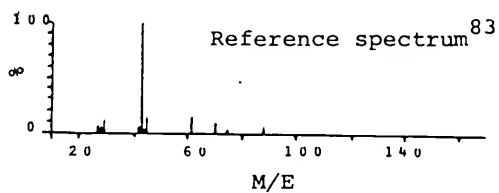
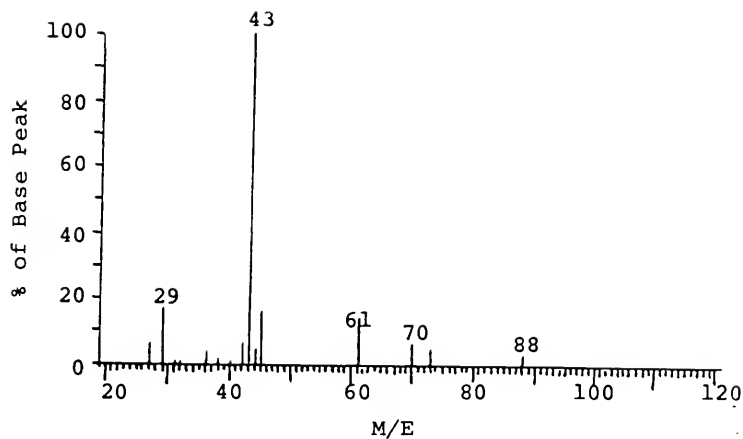


Figure 3-37. Mass Intensity Report for Ethyl Acetate

support that the tri-phosphine substituted triruthenium carbonyl cluster could be prepared. It has been reported that the formation of entirely the mono-phosphine substituted triruthenium carbonyl cluster can be facilitated in the presence of a  $\text{NaPh}_2\text{CO}$  catalyst.<sup>228</sup> A summary of all infrared data is provided in Table 3-12. It was observed that a color change from orange to yellow occurred upon exposure of the supported ruthenium carbonyl cluster to air. A similar observation has been reported for the air oxidation of  $\text{Ru}_3(\text{CO})_{12}$  on alumina to mononuclear  $\text{Ru}(\text{II})$  species.<sup>229</sup> This color change was observed to be accompanied by a change in the infrared spectrum as shown in Figure 3-38 which can be explained by the formation of a mixture of mononuclear ruthenium species such as  $\text{PPh}_2\text{Ru}(\text{CO})_4$  and  $\text{Ru}(\text{CO})_5$ .

A color change from orange to white was observed upon exposure of the supported ruthenium cluster to the reaction gas mixture of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{HCl}(\text{g})$ . An explanation for this color change can be derived from the fragmentation of the original cluster into mono and dinuclear species. It has been reported that an increase in temperature from  $60^\circ\text{C}$  to  $150^\circ\text{C}$  under a carbon monoxide atmosphere can initiate the fragmentation of the triphosphine substituted triruthenium carbonyl cluster into phosphine substituted mononuclear carbonyl species.<sup>230</sup> It also has been reported that  $\text{Ru}_3(\text{CO})_{12}$  is oxidized in the presence of halogens to form the corresponding mononuclear species,  $\text{Ru}(\text{CO})_4\text{X}_2$ .<sup>231</sup> This

Table 3-12. A Summary of Infrared Data Obtained for the Supported Ruthenium Cluster System

Complex or Reaction	Infrared Data (cm <sup>-1</sup> )	Environment	Reference
Si $\beta$ -(PPh <sub>2</sub> ) <sub>3</sub> Ru <sub>3</sub> (CO) <sub>9</sub>	2066 (vw), 2024 (w), 1967 (vs, br)	nujol	b (V)
[Ru <sub>3</sub> (CO) <sub>9</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	2044 (vw), 1978 (sh), 1967 (s, br)	benzene	232
[Ru <sub>3</sub> (CO) <sub>12</sub> + Si $\beta$ -PPh <sub>2</sub> ](I)	2095 (vw), 2060 (s)	nujol	b (Figs. 3-38, 3-39)
Ru <sub>3</sub> (CO) <sub>4</sub> PPh <sub>3</sub>	2097 (m), 2046 (s), 2030 (sh), 2023 (sh), 2014 (s), 1996 (sh), 1986 (m), 1972 (sh), 1960 (sh)	cyclohexane	232
Ru <sub>3</sub> ( $\nu$ -H)(CO) <sub>10</sub> ( $\nu$ -E Si)	2107 (w), 2076 (s), 2066 (s), 2026 (s), 1991 (m)	nujol	233
(I) + air	2060 (vs), 2030 (w), 1998 (vs)	nujol	b (Fig. 3-38)
(I) + H <sub>2</sub> , CO, HCl	2134 (s), 2063 (vs), 2030 (s), 1980 (m)	nujol	b (Figs. 3-39, 3-40)
Si $\beta$ -PPh <sub>2</sub> Ru(CO) <sub>4</sub>	2059, 1995, 1952	toluene	234
Si $\beta$ -PPh <sub>2</sub> Ru(CO) <sub>3</sub> PPh <sub>3</sub>	1900	toluene	234
Ru(CO) <sub>5</sub>	2035, 1999	decalin	235
Ru <sub>3</sub> (CO) <sub>10</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2078, 2024, 1999	decalin	235
Si $\beta$ -PPh <sub>2</sub> Ru(CO) <sub>4</sub>	2045 (m), 1990 (s), 1940 (sh)	wafer	230
Ru(CO) <sub>4</sub> Cl <sub>2</sub>	2185 (w), 2135 (s), 2115 (m), 2077 (s)	Et <sub>2</sub> O	236, 231
Ru(CO) <sub>2</sub> Cl <sub>2</sub>	2063 (s), 1989 (s)	CHCl <sub>3</sub>	236
PPh <sub>3</sub> Ru(CO) <sub>3</sub> Cl <sub>2</sub>	2133 (m), 2075 (s), 2033 (m)	C <sub>6</sub> H <sub>12</sub>	236
[PPh <sub>3</sub> Ru(CO) <sub>2</sub> Cl <sub>2</sub> ] <sub>2</sub>	2076 (s), 2016 (s)	CHCl <sub>3</sub>	236
RuCl <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2062 (vs), 2001 (vs)	nujol	b (VI)
[RuCl <sub>2</sub> (CO) <sub>3</sub> ] <sub>2</sub>	2145 (s), 2089 (m), 2067 (vs), 2025 (m)	nujol	b (VII), 231
[(RuCl <sub>2</sub> (CO) <sub>3</sub> ] <sub>2</sub> + Al $\beta$ -PPh <sub>2</sub> ](II)	2132 (s), 2054 (vs), 2024 (w), 1991 (vs)	nujol	b (Figs. 3-40, 3-41)
(II) + air	2087 (w), 2059 (vs), 2024 (w), 1993 (vs)	nujol	b (VIII)
(II) + H <sub>2</sub> , CO, HCl	2133 (s), 2057 (vs), 2018 (w), 1994 (vs)	nujol	b (Fig. 3-41)

b = This work; (V-VIII) = location of spectrum in appendix B;  
 vs = very strong; s = strong; ms = medium strong; m = medium;  
 w = weak; vw = very weak; br = broad; sh = shoulder.

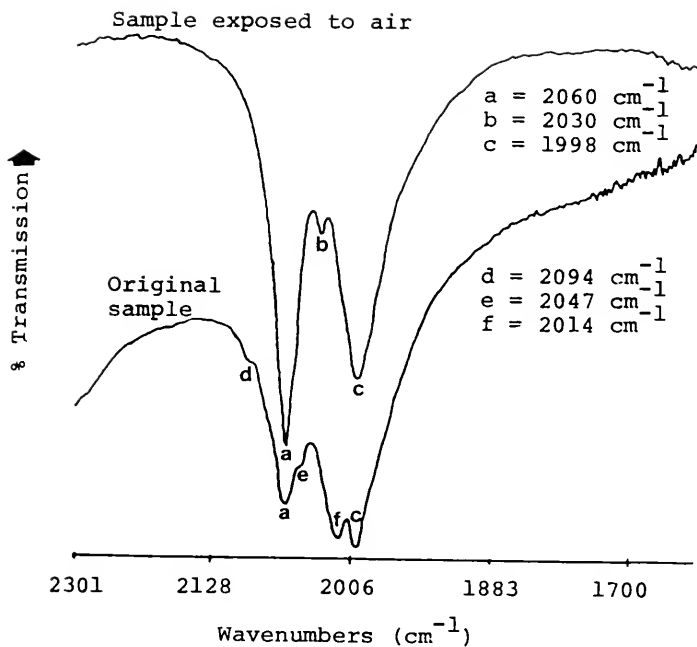


Figure 3-38. Infrared Spectrum of a Mixture of the Supported Ruthenium Clusters Exposed to Air

mononuclear species,  $\text{Ru}(\text{CO})_4\text{X}_2$ , can react further to produce a variety of white mono and dinuclear ruthenium carbonyl complexes.<sup>236</sup> The infrared spectrum that was obtained for the white supported complex as shown in Figure 3-39 can be assigned to the mononuclear complex,  $\text{Z-PPh}_2\text{Ru}(\text{CO})_3\text{Cl}_2$ . The carbonyl absorption observed in the infrared spectrum at  $1980\text{ cm}^{-1}$  suggests the presence of a small amount of another ruthenium complex, such as  $\text{Ru}(\text{CO})_2\text{Cl}_2$ . It is also possible that a supported dinuclear carbonyl species is present. This contention is supported in that the reaction between  $[\text{RuCl}_2(\text{CO})_3]_2$  and the phosphinated support yields a complex with an infrared spectrum which is similar to that observed for the supported triruthenium cluster after being exposed to the reactant gas mixture as shown in Figure 3-40. The infrared spectrum of this supported dinuclear complex as shown in Figure 3-41 was observed to remain unchanged upon exposure to the reactant gas mixture. This suggests that a chloro-ruthenium compound is the resulting carbonyl complex present under  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  at low temperatures.

Interpretation of the previous infrared spectra is complicated by the possibility that the stabilization of various mononuclear fragments which result from the decomposition of the triruthenium cluster may occur under the employed reaction conditions. It has been reported that  $\text{Ru}_3(\text{CO})_{12}$  decomposes on a silica gel support to form off white colored mononuclear species as shown in Figure 3-42.<sup>233</sup> The similarities between the reported carbonyl

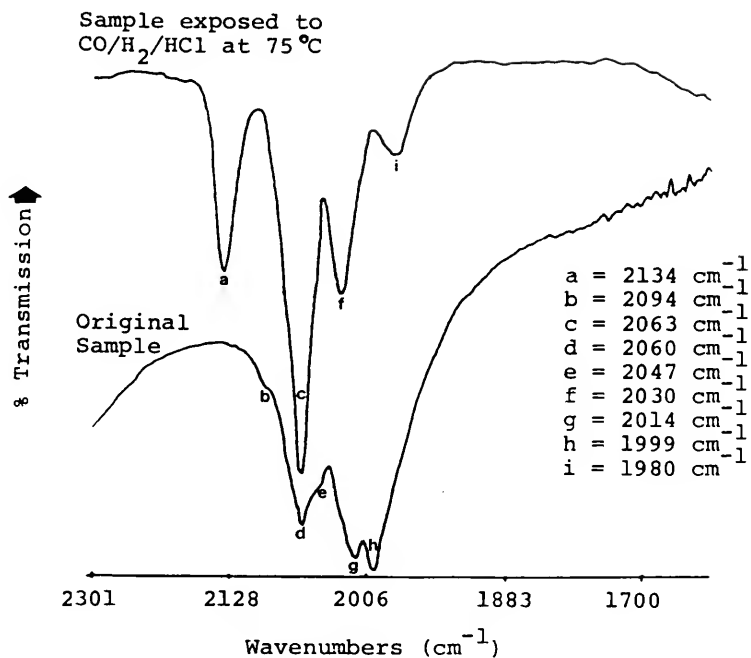


Figure 3-39. Infrared Spectrum of the Supported Ruthenium Clusters Exposed to CO, H<sub>2</sub> and HCl(g) at 75°C

**A** =  $\text{Ru}_3(\text{CO})_{12}$  +  $\exists\text{-PPh}_2$  exposed to  
 $\text{CO}/\text{H}_2/\text{HCl}$  at  $75^\circ\text{C}$

**B** =  $(\text{RuCl}_2(\text{CO})_3)_2$  +  $\exists\text{-PPh}_2$

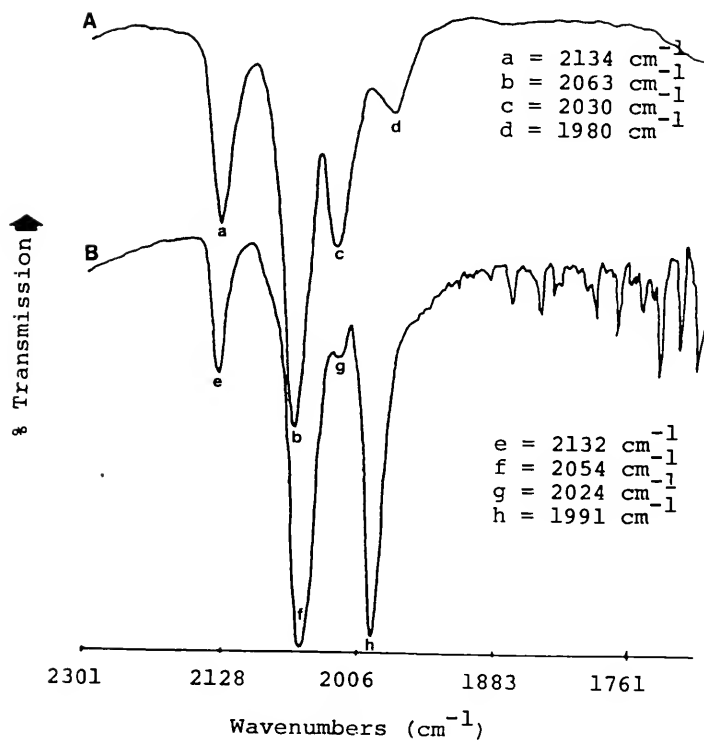


Figure 3-40. A Comparison of the Infrared Spectrum of the Supported Ruthenium Clusters With that of Supported  $[\text{RuCl}_2(\text{CO})_3]_2$



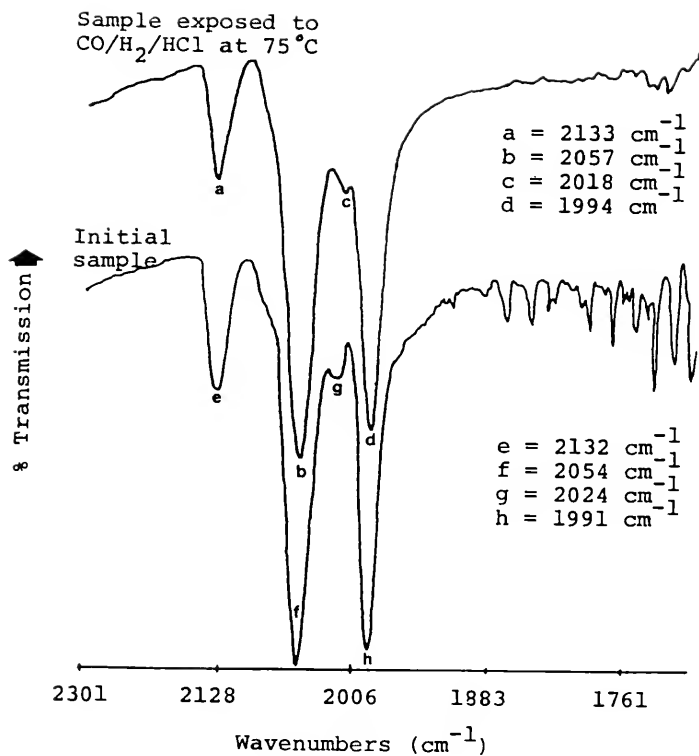


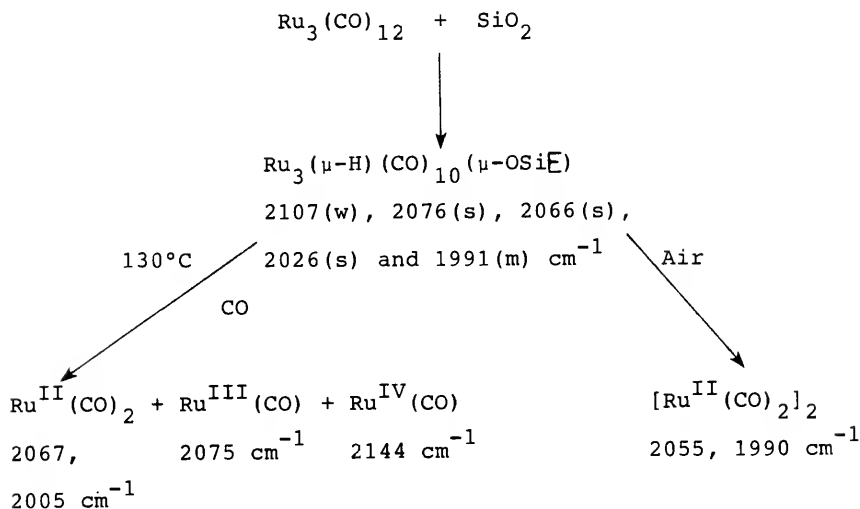
Figure 3-41. Infrared Spectrum of Supported  $[\text{RuCl}_2(\text{CO})_3]_2$  Before and After Exposure to CO, H<sub>2</sub> and HCl(g) at 75°C

absorptions for these ruthenium carbonyl fragments and those observed for the triruthenium cluster exposed to  $H_2$ , CO and  $HCl(g)$  suggests the possibility of the presence of a mixture of ruthenium fragments and ruthenium chloro-carbonyl complexes.

A mechanism for the formation of 2-carbon products can only be speculated upon at this time. It is possible that some of these products arise from the presence of surface ethoxide groups that were formed during the phosphination of the support. These surface ethoxide groups were exchanged for  $\beta\text{-OC}_3\text{H}_7$  groups by stirring the supported ruthenium complex in propanol in an attempt to determine the extent in which the  $\beta\text{-OC}_2\text{H}_5$  groups affect the activity for ethyl chloride formation. It was demonstrated by infrared spectroscopy that the supported ruthenium cluster had not been affected by this procedure. The activity for ethyl chloride formation at  $75^\circ\text{C}$  under CO,  $H_2$  and  $HCl(g)$  for this supported complex was found to be similar to the previously reported activity of  $1.16 \times 10^{-9}$  moles ethyl chloride  $\text{sec}^{-1} \text{g}^{-1}$ . This suggests that the ethoxide groups play a minor role in the formation of the ethyl chloride. It should be noted that a considerable amount of propyl chloride was observed to form in this reaction. It is suggested that this propyl chloride arises from attack of  $HCl(g)$  upon the absorbed propanol present in the support.

A more likely possibility for the formation of ethyl chloride arises from the addition of  $HCl(g)$  across the

double bond in ethylene over the supported cluster. Recall that ethylene and ethyl chloride are trace impurities found



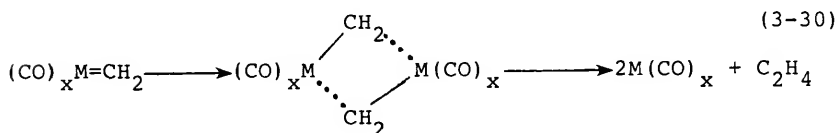
s = strong; m = medium; w = weak.

Figure 3-42. Fragmentation of  $\text{Ru}_3(\text{CO})_{12}$  on a Silica Gel Support

in the technical grade  $\text{HCl}(\text{g})$ . It is possible that the supported ruthenium complex is more efficient at converting ethylene to ethyl chloride than the other supported metal systems that were investigated. If electronic grade  $\text{HCl}(\text{g})$ , which did not contain any ethylene impurity, was used in place of the technical grade  $\text{HCl}(\text{g})$ , the formation of ethylene was observed to occur as identified by gas

chromatography. The formation of ethylene is most likely occurring by the conversion of bound carbonyl groups during the decomposition of the supported ruthenium cluster. It has been reported that  $\text{Ru}_3(\text{CO})_{12}$  reacts with  $\text{AlH}_3$  in THF to produce predominantly methane and ethylene in a ratio of 1:1.7.<sup>237</sup> This reaction was shown to be stoichiometric in that only approximately 10% of the bound carbonyl groups in  $\text{Ru}_3(\text{CO})_{12}$  were found to be converted.<sup>237</sup> It was suggested that the formation of ethylene proceeded through a carbenoid metal intermediate as shown in Equation 3-30.

One last possibility for the formation of these 2-carbon products is the reduction of carbon monoxide through a mechanism similar to that discussed in Figure 3-27 for the formation of methyl chloride in the iridium system. In this mechanism the formation of 2-carbon products could result from the insertion of carbon monoxide into a hydroxymethyl intermediate. Attempts to incorporate



carbon-13 into ethyl chloride from  $^{13}\text{CO}$  have been inconclusive. It is proposed that the formation of the two-carbon products in the supported ruthenium cluster system results from the conversion of carbonyl ligands in the

cluster during decomposition or fragmentation on the support and from the reduction of carbon monoxide.

### Summary

The previously reported results<sup>148</sup> for the formation of methyl chloride from CO, H<sub>2</sub> and HCl(g) in the supported iridium cluster system were shown to be clouded by the presence of adsorbed 2-methoxyethanol on the support. This adsorbed 2-methoxyethanol was shown to be cracked by HCl(g) to methyl chloride at 75°C. Attempts to remove this adsorbed 2-methoxyethanol from the system by varying the washing and drying procedures during the preparation of the catalyst were unsuccessful. Since this adsorbed 2-methoxyethanol was difficult to remove, attention was turned to the synthesis of the supported iridium clusters in other solvents, such as 2-ethoxyethanol or toluene.

The clusters synthesized in either 2-ethoxyethanol or toluene were observed to exhibit an activity of  $1.9 \times 10^{-12}$  moles CH<sub>3</sub>Cl sec<sup>-1</sup> g<sup>-1</sup> at 75°C. The decomposition of inherent impurities in the system were observed to lead to the formation of trace quantities of methyl chloride in the initial stages of the reaction. It was proposed that the major contributor to the initial formation of methyl chloride ( $1.9 \times 10^{-12}$  moles CH<sub>3</sub>Cl sec<sup>-1</sup> g<sup>-1</sup>) in the supported iridium cluster system is the conversion of iridium bound carbonyl groups during the support induced fragmentation of the cluster. It was suggested that as the reaction time progressed the percentage of methyl chloride

produced from the reduction of synthesis gas would increase.

Infrared spectroscopy was used to characterize the supported iridium clusters and the fragmentation products that resulted upon exposure to CO, H<sub>2</sub> and HCl(g) at various temperatures. The synthesis of predominantly the mono-phosphine cluster was observed only to result in a 2-methoxyethanol solvent. It was suggested that this cluster could also be formed if Ir<sub>4</sub>(CO)<sub>12</sub> was reacted with a phosphinated support which had been previously silanated with Cl<sub>2</sub>SiPh<sub>2</sub>. In this case, multiple phosphine substitution in Ir<sub>4</sub>(CO)<sub>12</sub> would be sterically hindered by the presence of  $\text{SiPh}_2$  groups. All of the supported iridium carbonyl clusters were observed to exhibit a predominant infrared absorption centered at either 2069 or 2040 cm<sup>-1</sup> after exposure to CO, H<sub>2</sub> and HCl(g) at 75°C. A high iridium concentration of the support was found to lead to the observation of the 2069 cm<sup>-1</sup> infrared absorption. The 2040 cm<sup>-1</sup> absorption was found to correlate with the presence of a low iridium concentration. The infrared absorptions observed for the supported clusters (Low % Ir) at 2048, 1734 and 1719 cm<sup>-1</sup> were assigned to the formation of a phosphine bound multinuclear species containing bridging carbonyl and chloride ligands. This multinuclear complex was suggested to be similar to  $[\text{Ir}_2(\text{CO})_4\text{Cl}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{BPh}_4]$ . The infrared absorptions observed for the supported clusters (High % Ir) were assigned to a mixture of the multinuclear complex and

$\text{IrCl}(\text{CO})_3$ . The conversion of the multinuclear complex to  $\text{IrCl}(\text{CO})_3$  was observed as the reaction temperature was increased. Similar results were observed for reactions employing either  $\text{IrCl}(\text{CO})_3$  or Vaska's complex on a phosphinated support. It is suggested that the multinuclear species is active towards the formation of methyl chloride from synthesis gas and  $\text{HCl}(\text{g})$ . It also was shown that  $\text{IrCl}(\text{CO})_3$  is inactive as a CO reduction catalyst under the employed reaction conditions.

The gradual formation of metallic iridium was observed by infrared spectroscopy at temperatures exceeding  $200^\circ\text{C}$ . The conversion of synthesis gas and  $\text{HCl}(\text{g})$  to alkyl chloride in the presence of iridium metal catalysts at temperatures of greater than  $200^\circ\text{C}$  has previously been described by Vannice.<sup>194</sup> It was shown that iridium metal is inactive towards the formation of methyl chloride below  $200^\circ\text{C}$ . Thus it was suggested that metallic iridium does not play a major role below  $200^\circ\text{C}$  in the supported iridium carbonyl cluster system.

Finally, a mechanism was proposed for the formation of methyl chloride in the supported iridium carbonyl cluster system. The initial activity was dominated by methyl chloride formed through the degradation of the supported iridium cluster and by the decomposition of inherent system impurities. As the reaction time progressed the system's activity was suggested to be dependent upon the conversion of CO,  $\text{H}_2$  and  $\text{HCl}(\text{g})$ . The mechanism for the reduction of

carbon monoxide was based upon the formation of formyl, formaldehyde and hydroxymethyl intermediates.

This investigation concluded with the examination of various other phosphine supported metal carbonyl systems. It was observed by infrared spectroscopy that the supported osmium, cobalt and iron carbonyl systems formed  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{CoCl}_2$  and  $\text{Fe}(\text{CO})_5$ , respectively, upon exposure to  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCl}(\text{g})$  at  $75^\circ\text{C}$ . A supported ruthenium carbonyl cluster was found to produce ethyl chloride ( $1.16 \times 10^{-9}$  moles  $\text{C}_2\text{H}_5\text{Cl sec}^{-1} \text{ g}^{-1}$ ) along with a variety of other 2-carbon products. The supported triruthenium cluster was observed by infrared spectroscopy to form ruthenium chlorocarbonyl complexes upon exposure to  $\text{H}_2$ ,  $\text{CO}$  and  $\text{HCl}(\text{g})$  at  $75^\circ\text{C}$ . It was proposed that the two-carbon products were formed from the bound carbonyl ligands during cluster fragmentation and from the reduction of carbon monoxide. A mechanism similar to that for the supported iridium carbonyl system was suggested. In this case, insertion of  $\text{CO}$  into the  $\text{Ru-C}$  bond in the hydroxymethyl intermediate could lead to the two-carbon products. In general, it is suggested that a change in either the metal nucleophilicity or the supports acidity may alter the activity and selectivity of the system.



## CHAPTER IV

### CONCLUSION

The primary objective of the preceding two studies was to investigate the feasibility of binding and activating both carbon dioxide and carbon monoxide. The first study demonstrated that the binding of carbon dioxide was influenced by the nucleophilicity of the metal center in the transition metal carbonyl anion. An extension of this work into the low pressure reduction of carbon dioxide by  $\text{Re}_2(\text{CO})_{10}$  in methanol to methyl formate concluded that the carbon dioxide most likely is initially converted to carbon monoxide through a reverse water-gas shift reaction. It is this carbon monoxide that is reduced under the employed reaction conditions to methyl formate.

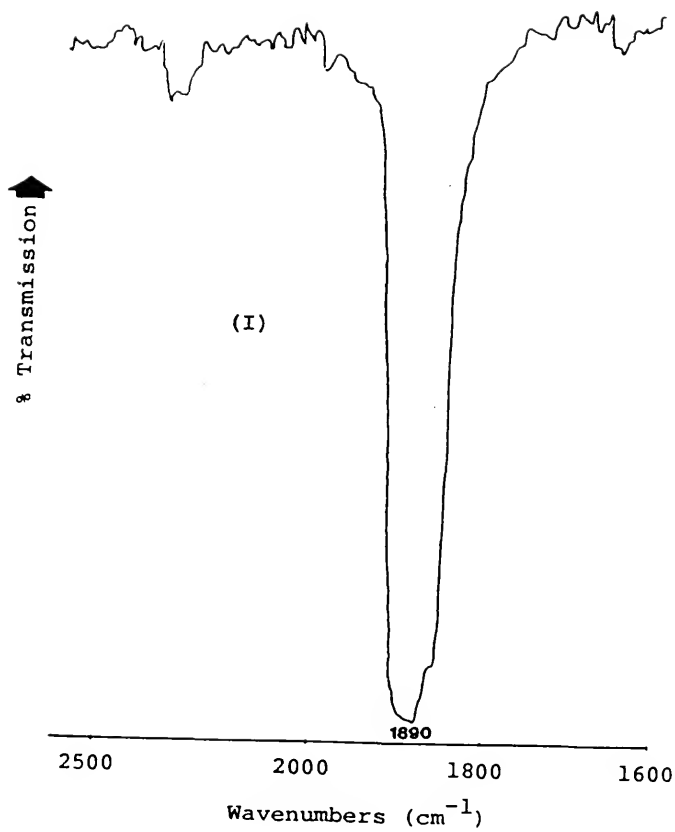
The feasibility of reducing carbon monoxide was investigated further in an acidic system employing a supported iridium catalyst. It was concluded that the conversion of synthesis gas and  $\text{HCl(g)}$  to alkyl halides proceeds under low temperatures and pressures through the stabilization of discrete iridium carbonyl complexes. The formation of ethyl chloride and other two-carbon products in a supported ruthenium system demonstrated that a change in catalyst composition could affect the selectivity and activity of the reaction.

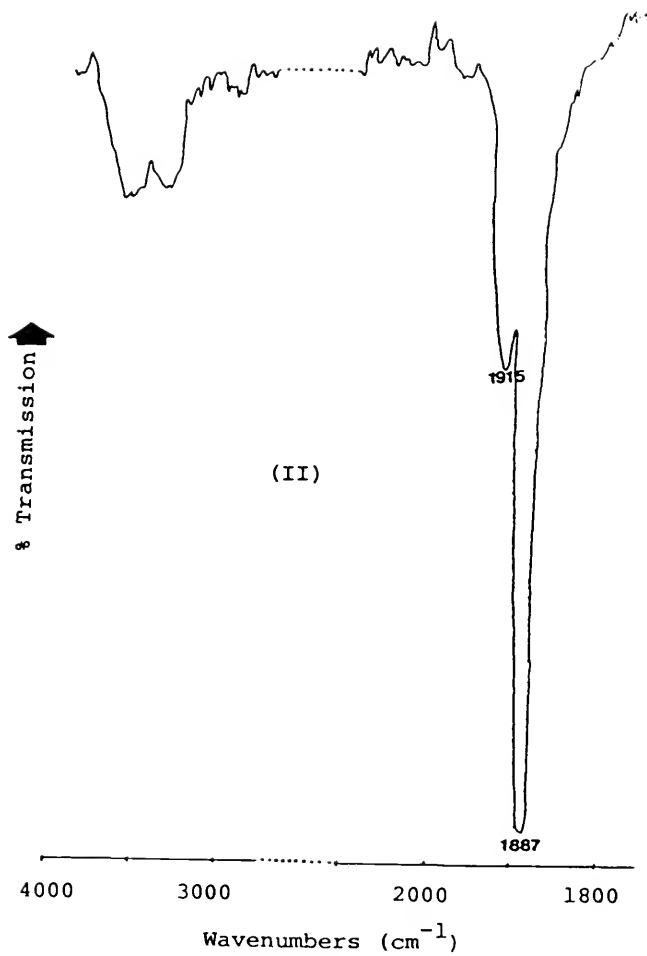
Although the preceding two studies are not processes which are ready for commercialization, they do further the understanding of the interaction between carbon dioxide and carbon monoxide with transition metal carbonyl complexes. The feasibility of reducing either carbon monoxide or carbon dioxide in the presence of transition metal carbonyl complexes has been demonstrated. This work suggests that it may be desirable to design catalysts for the sole purpose of reducing carbon dioxide to carbon monoxide. The further reduction of this carbon monoxide could be accomplished through a bifunctional interaction with an inorganic oxide support and a transition metal complex. In general, it is only through more work in this area that the overall goal of developing carbon dioxide and carbon monoxide as alternate carbon resources for chemical feedstocks and fuels may be realized.

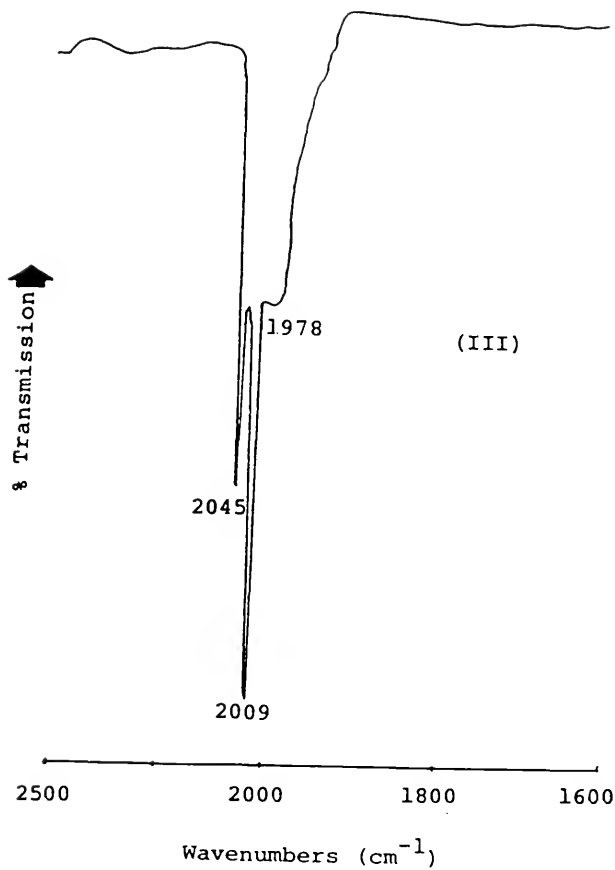
# APPENDIX A

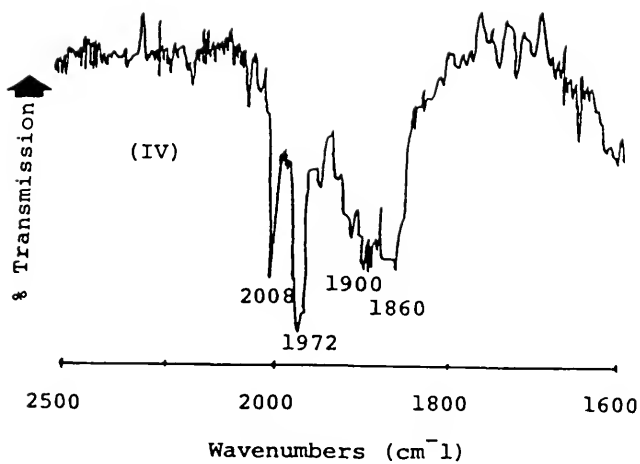
The following infrared spectra are meant as supplementary material for Chapter II. A list of the spectra included in this section is provided below.

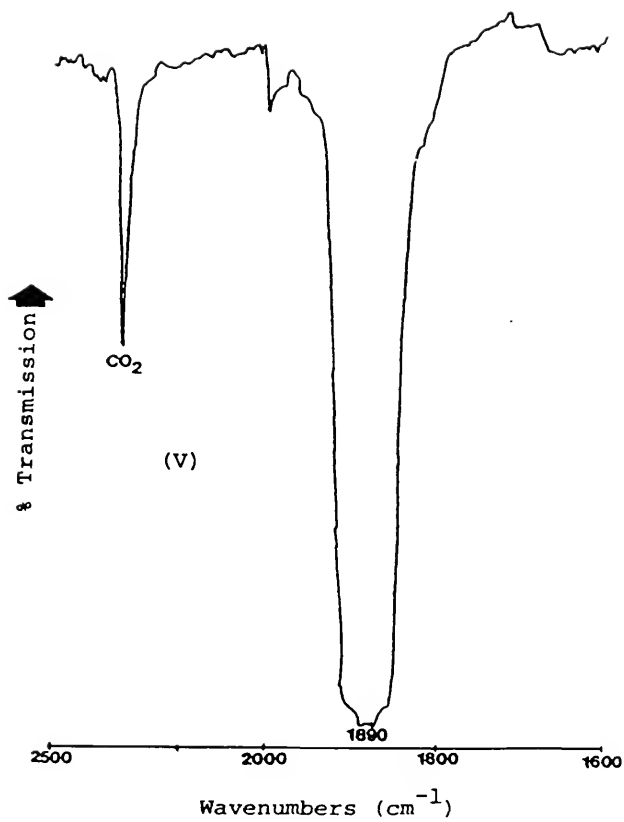
	<u>Page</u>
I. $\text{KCo}(\text{CO})_4$ . . . . .	195
II. $\text{K}[\text{HFe}(\text{CO})_4]$ . . . . .	196
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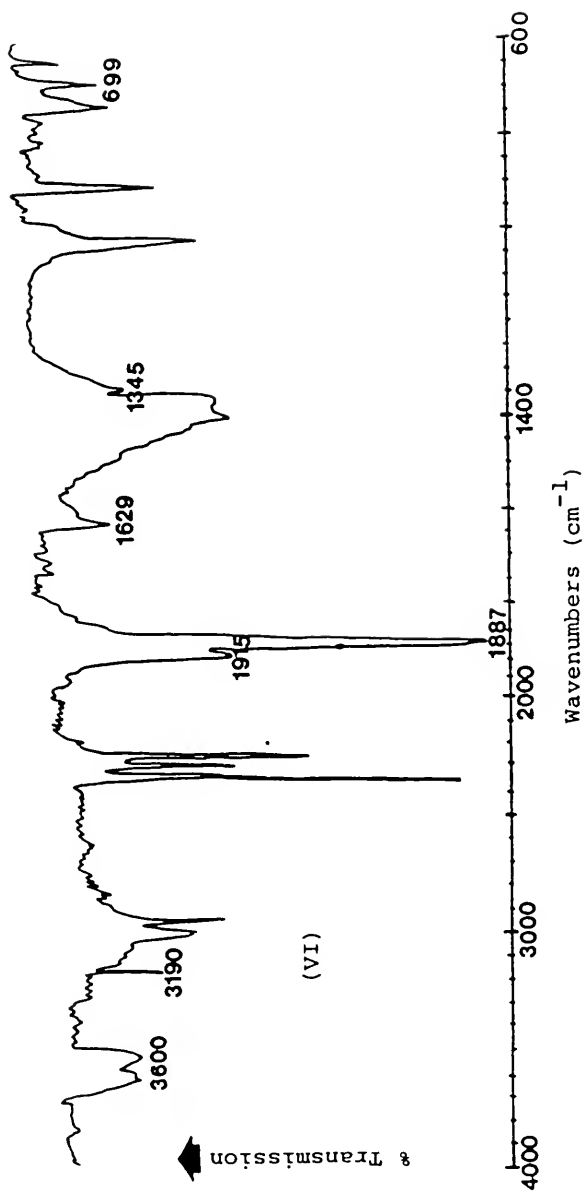


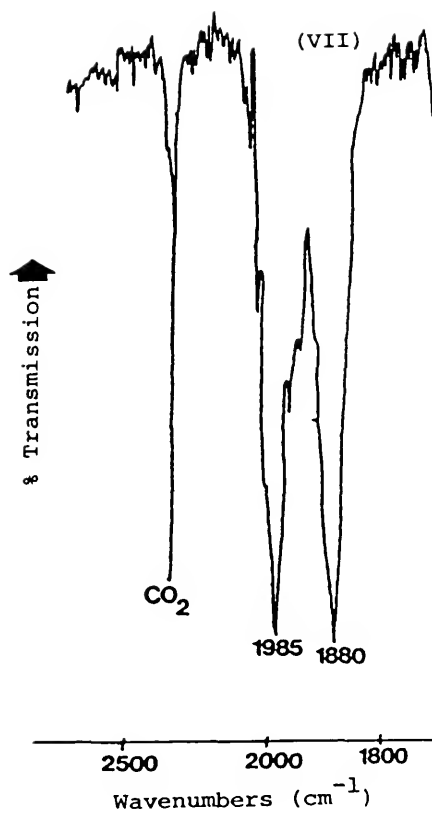


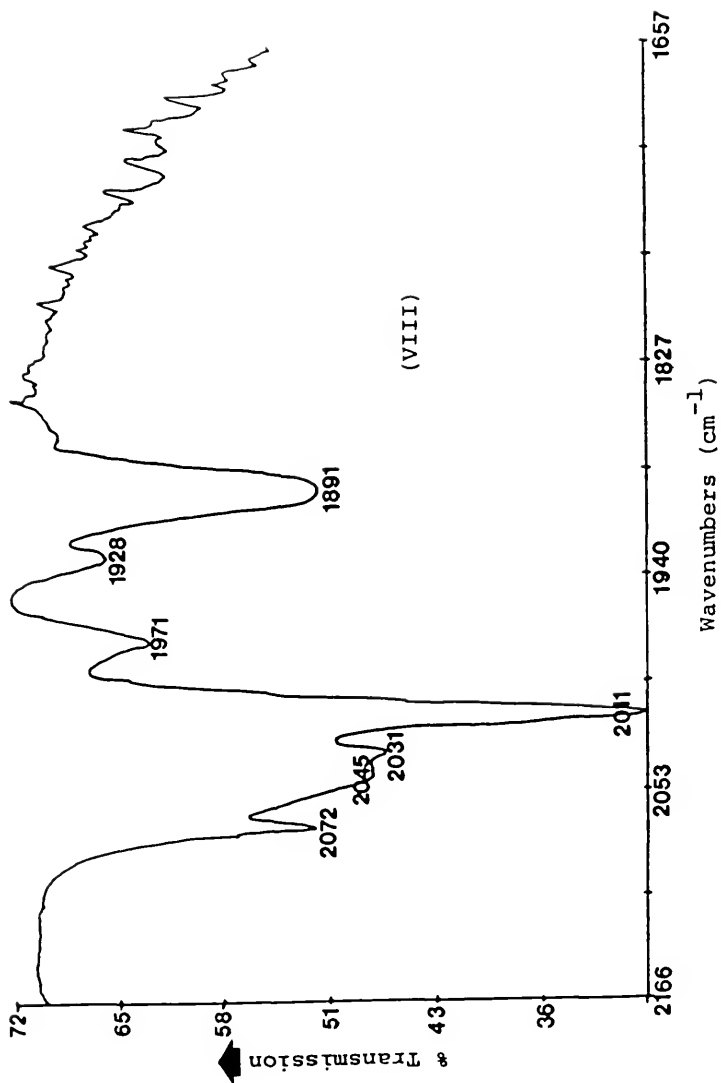


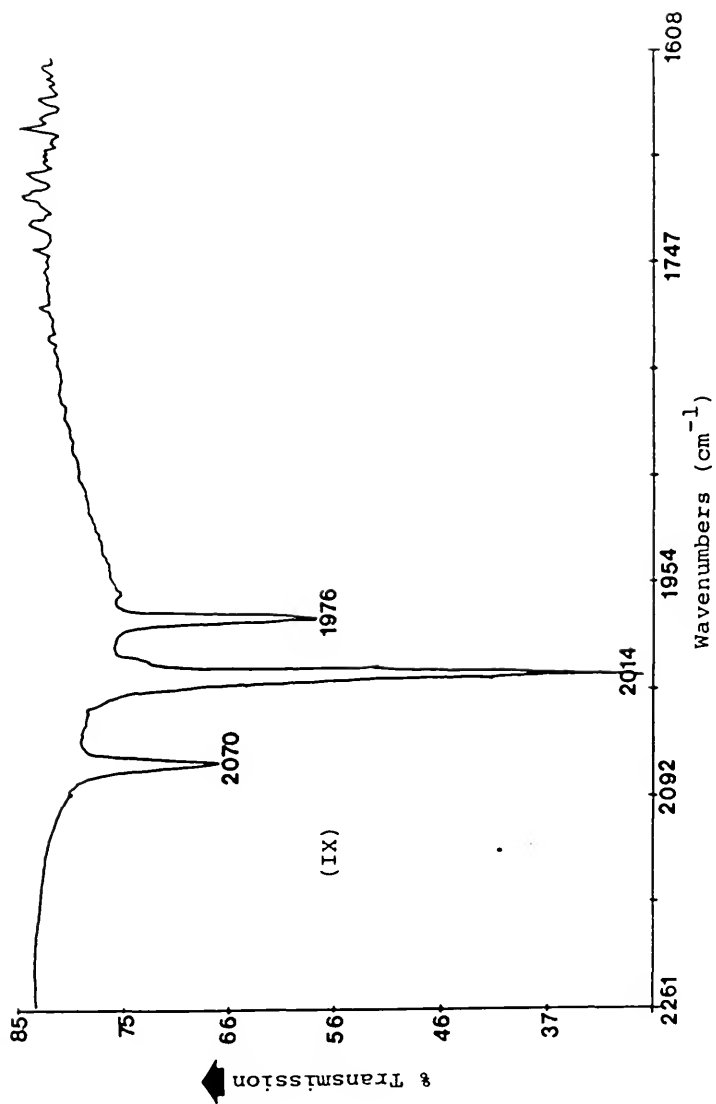


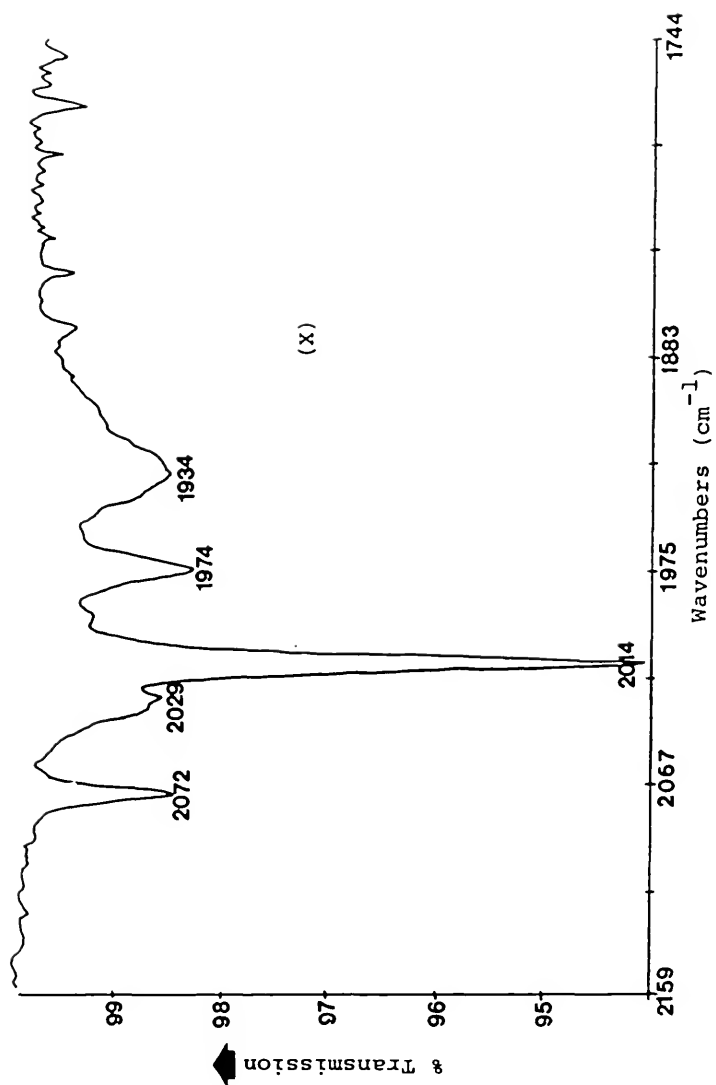


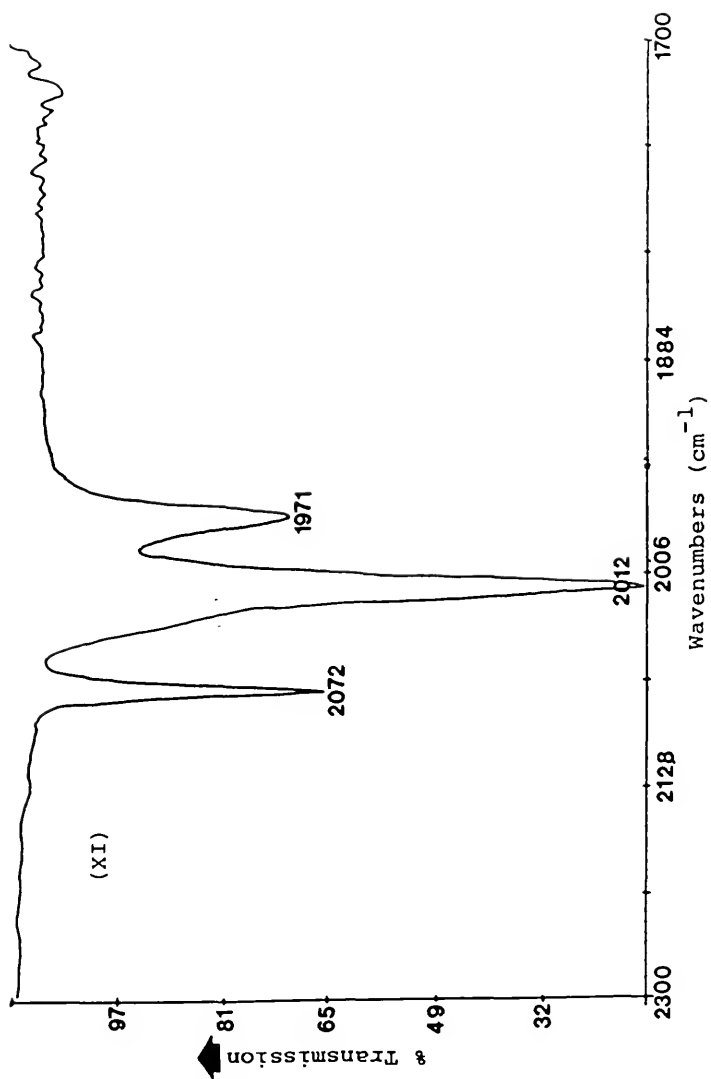


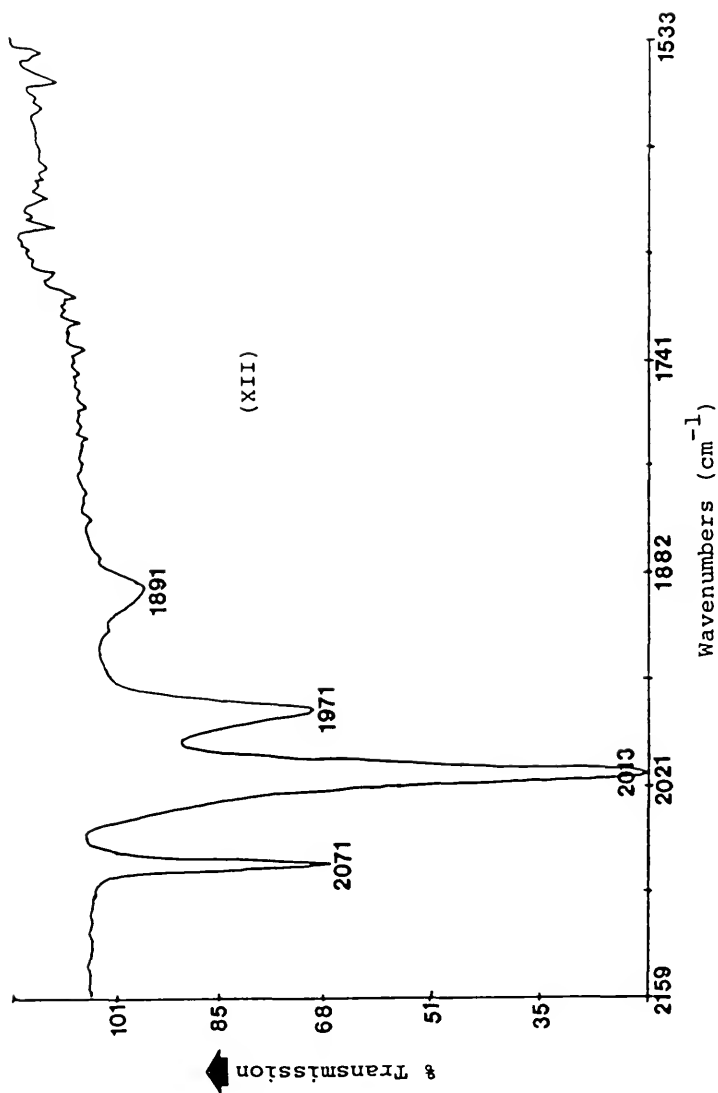


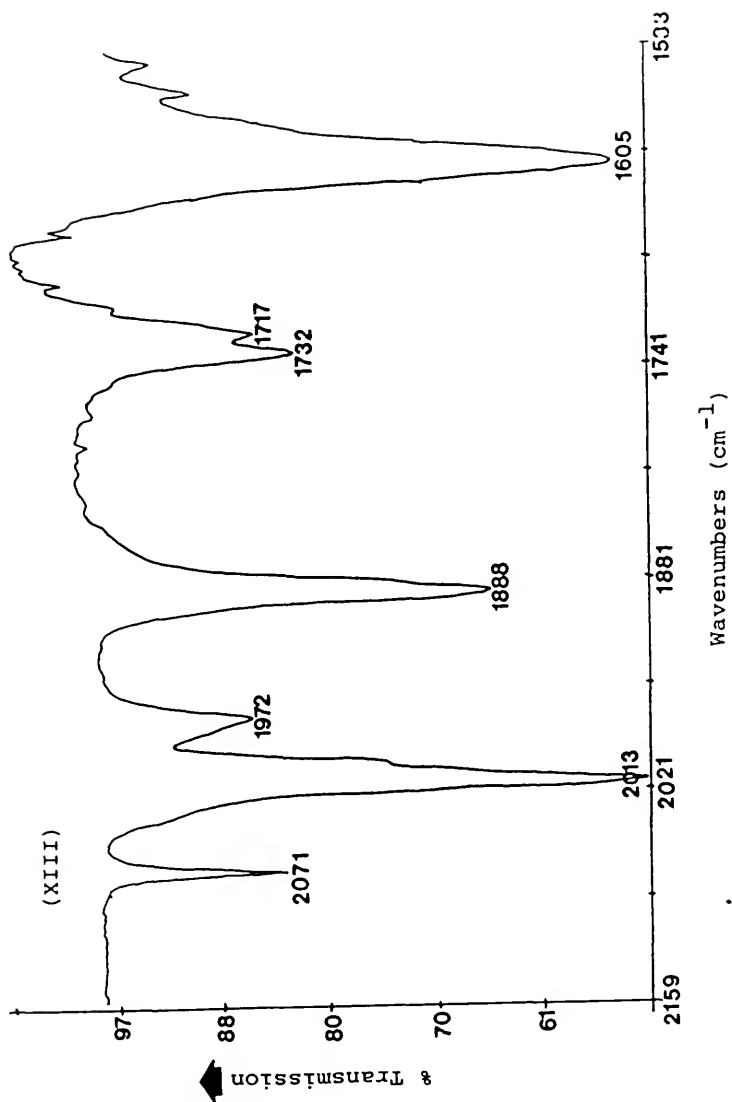




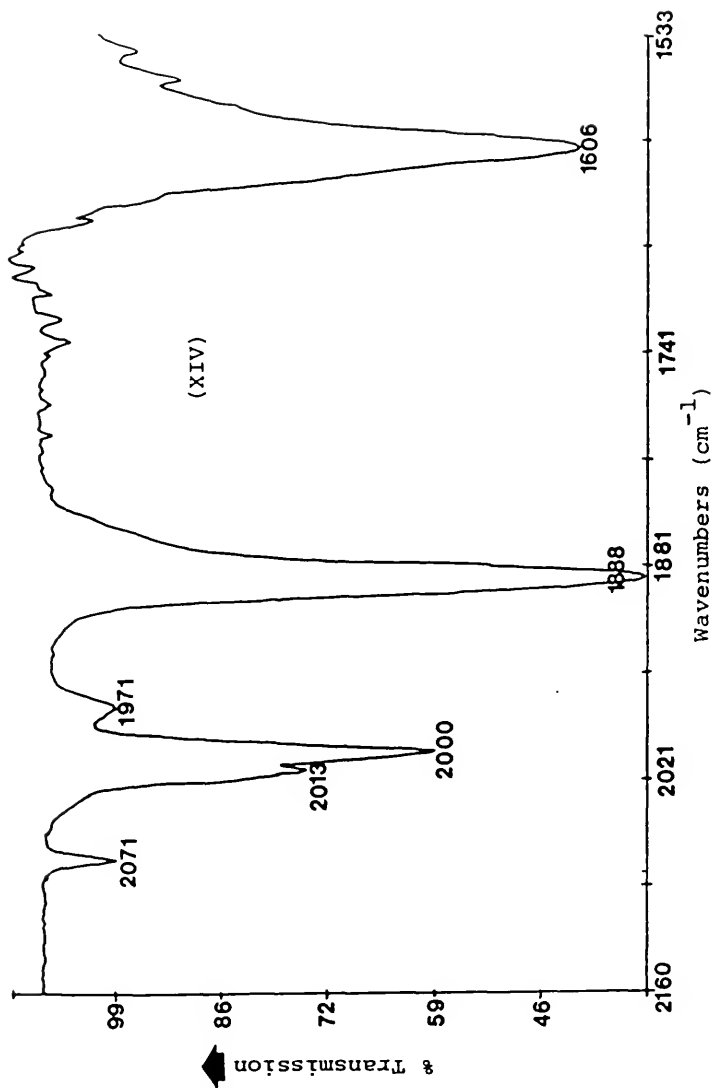


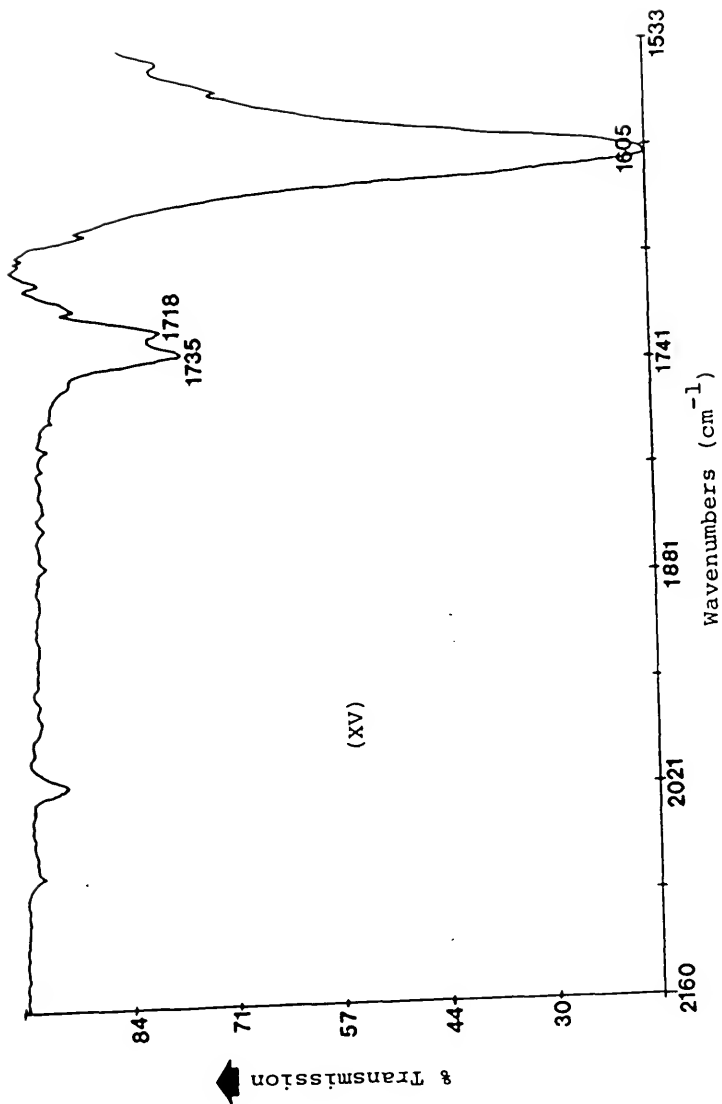


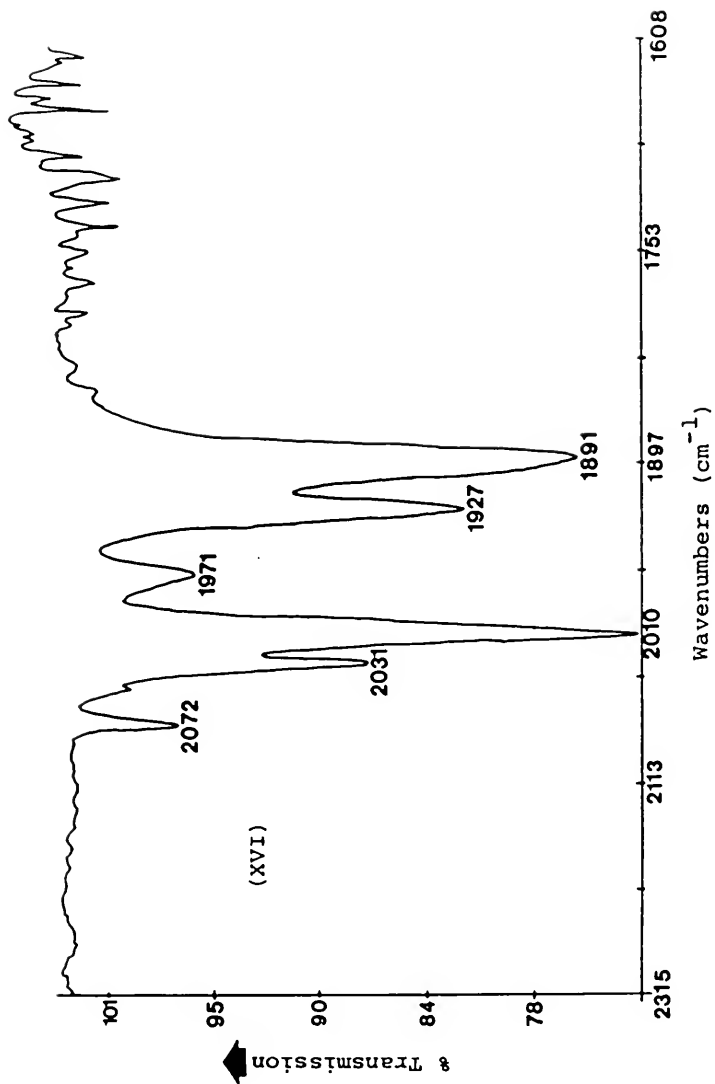








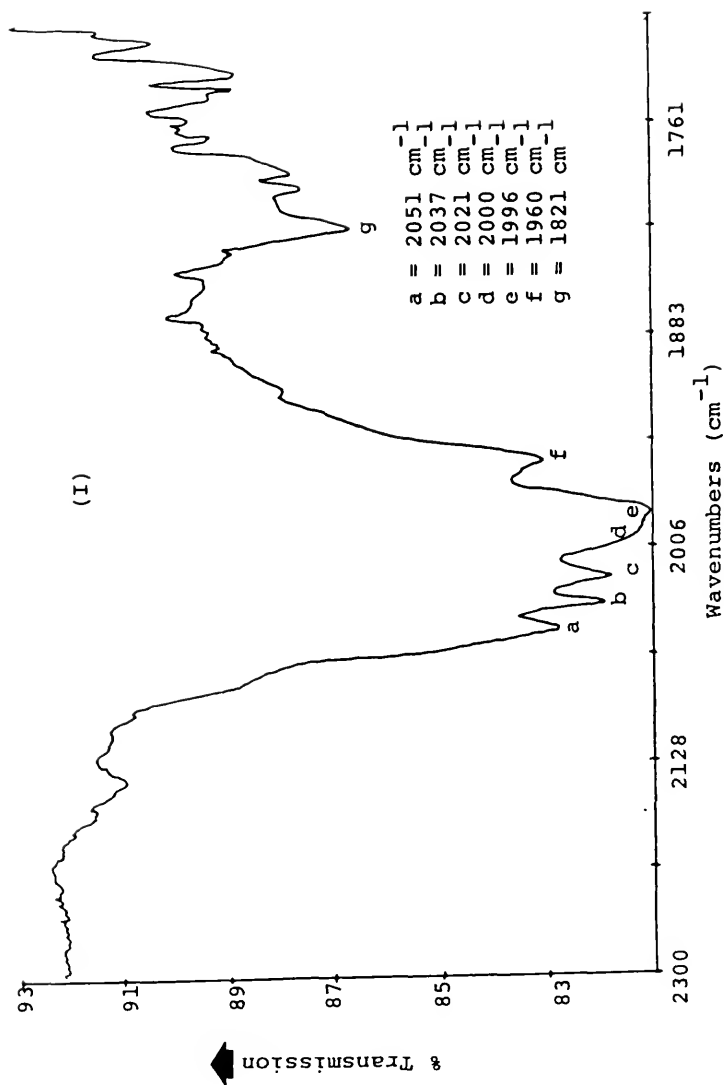


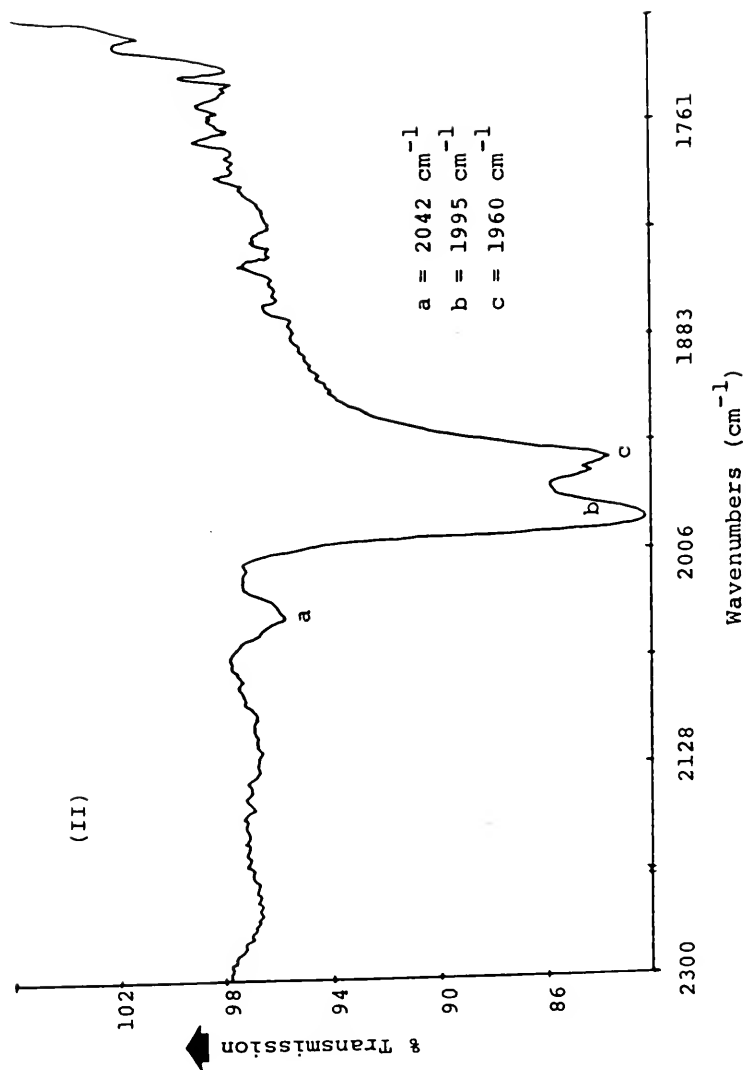


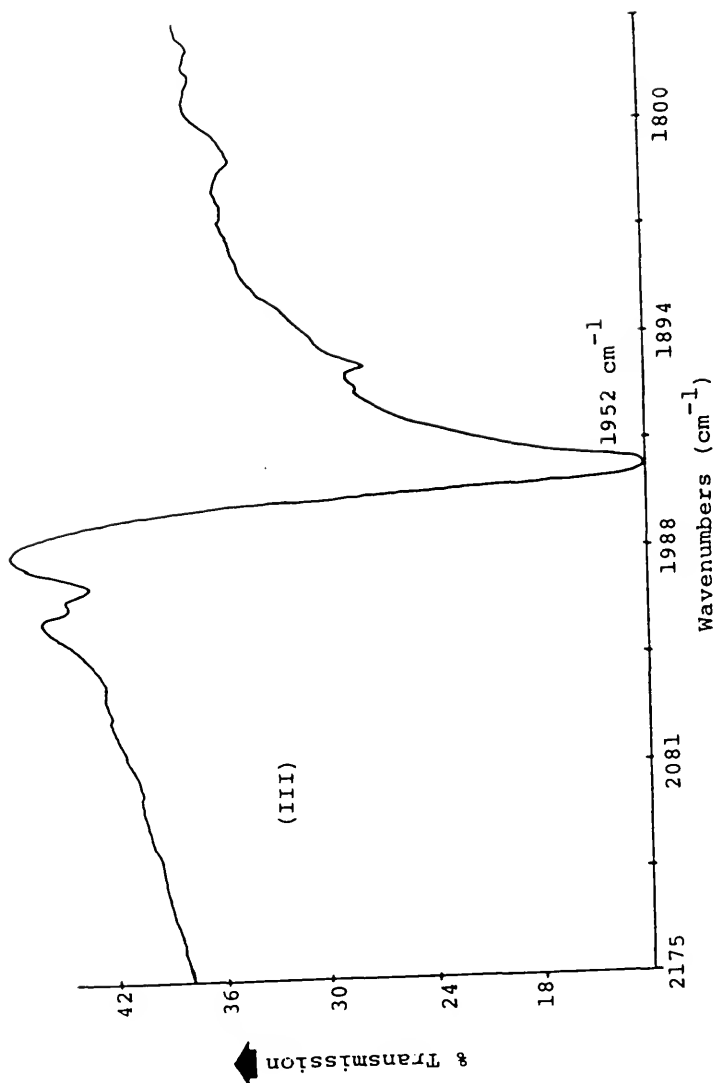
## APPENDIX B

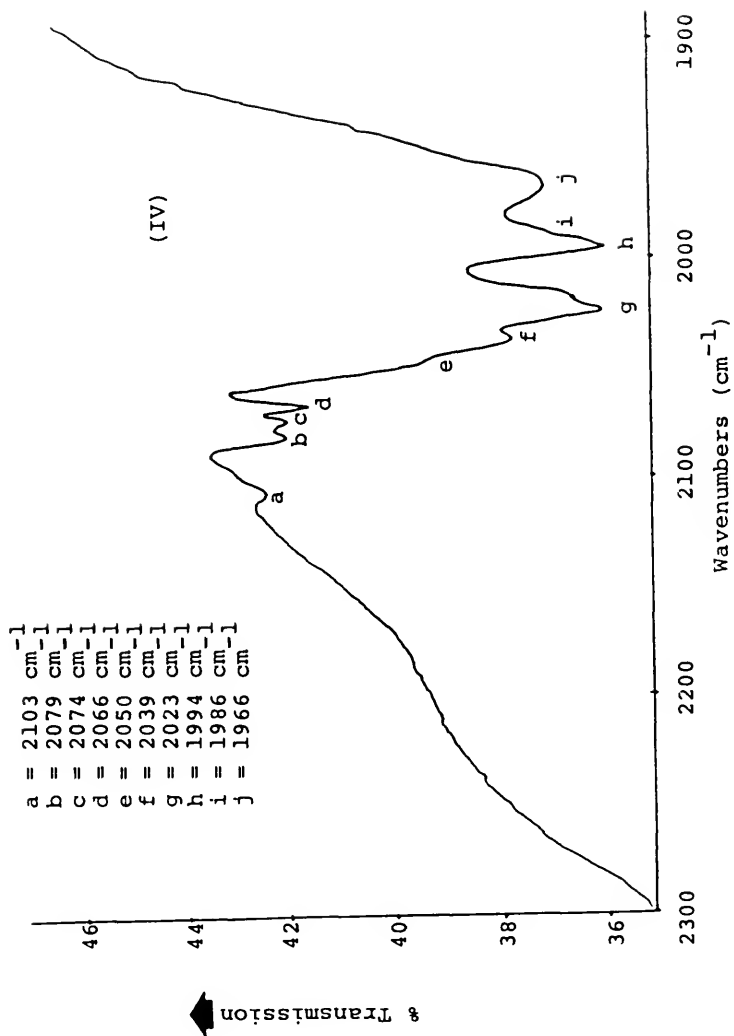
The following infrared spectra are meant as supplementary material for Chapter III. A list of the spectra included in this section is provided below.

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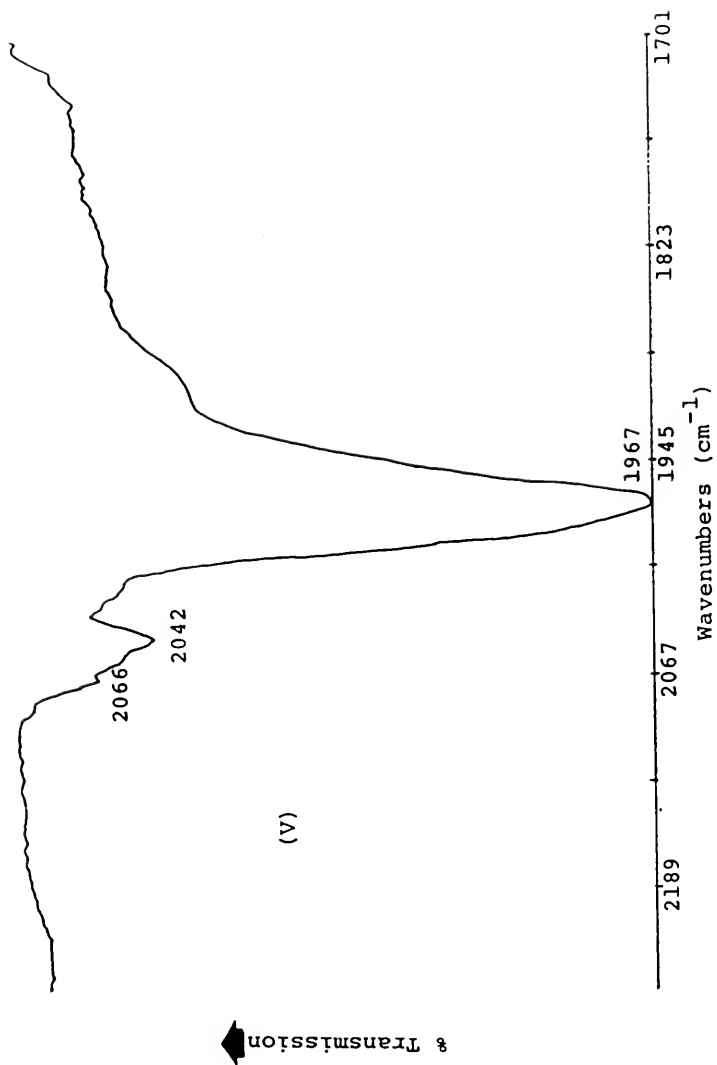


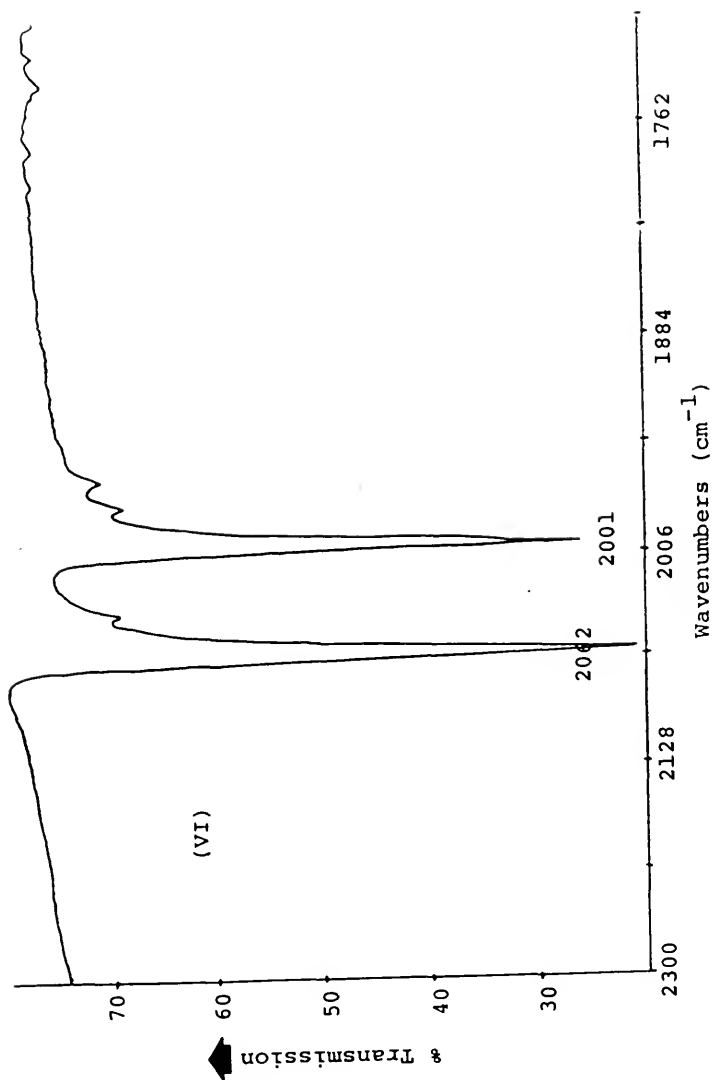


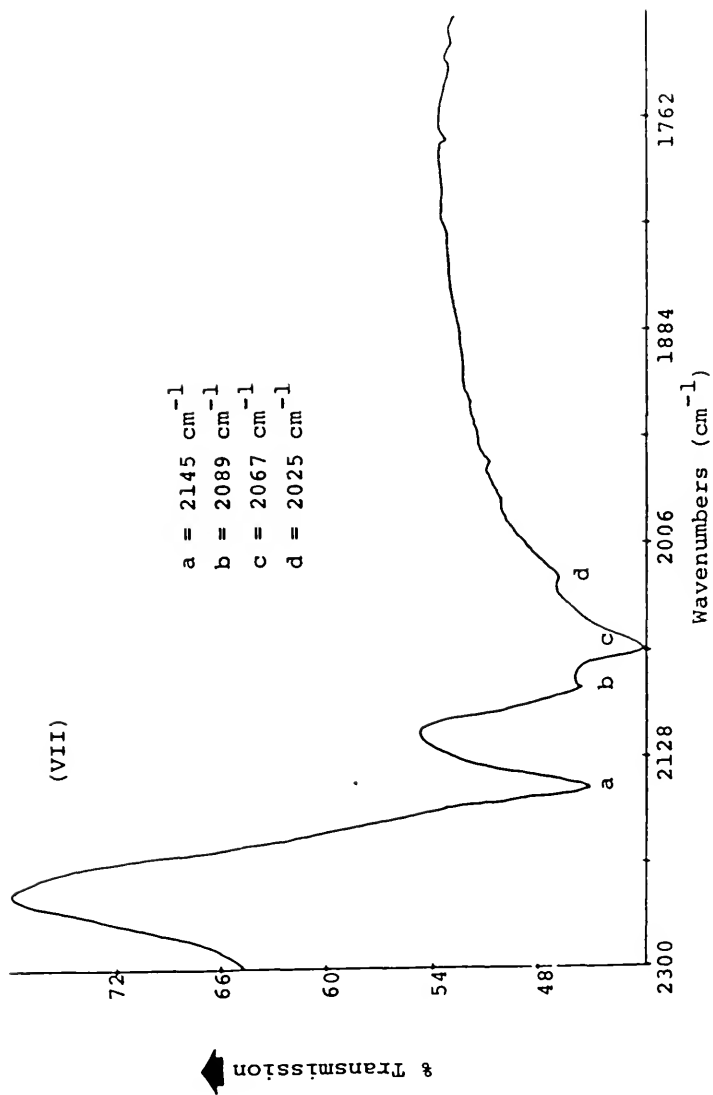


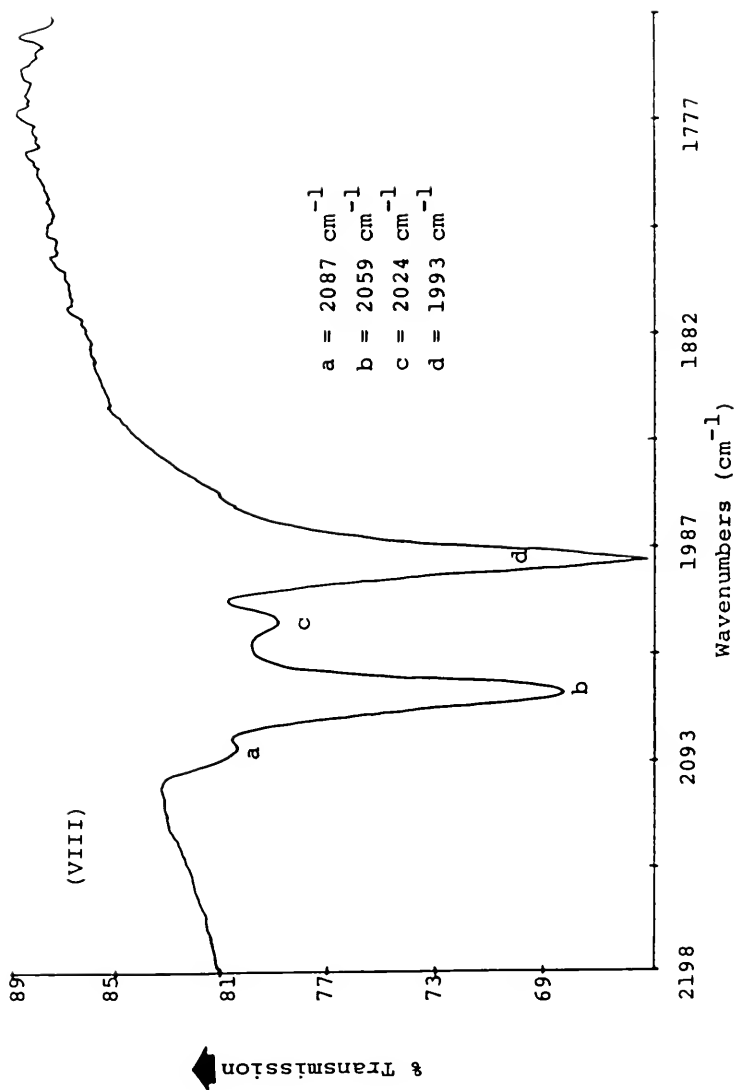












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#### BIOGRAPHICAL SKETCH

The author was born in Harrisburg, Pennsylvania, and grew up in Jamestown, New York. He graduated from Jamestown High School with honors in 1977. In 1981, he graduated magna cum laude from Clemson University. Upon graduation he was awarded the Mark Bernard Hardin Award for excellence in chemistry. His graduate studies were started at the University of Illinois immediately after receiving his B. S. in chemistry. After one year at the University of Illinois he transferred to the University of Florida with Dr. Drago and other members of his research group. Upon completion of his graduate studies he will begin his career in the employment of Dow Corning Corporation, Midland, Michigan. The author is listed as a co-inventor on U.S. Patent 4,538,011, entitled "Method for the Preparation of Halogen Substituted Methanes and Ethanes".


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Russell S. Drago  
Graduate Research Professor  
of Chemistry

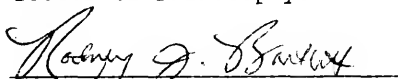
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David E. Richardson  
Assistant Professor of  
Chemistry

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Robert C. Stoufer  
Associate Professor of  
Chemistry

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Rodney J. Bartlett  
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

---

David N. Silverman  
Professor of Pharmacology  
and Therapeutics and of  
Biochemistry and Molecular  
Biology

This thesis was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Dean, Graduate School

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